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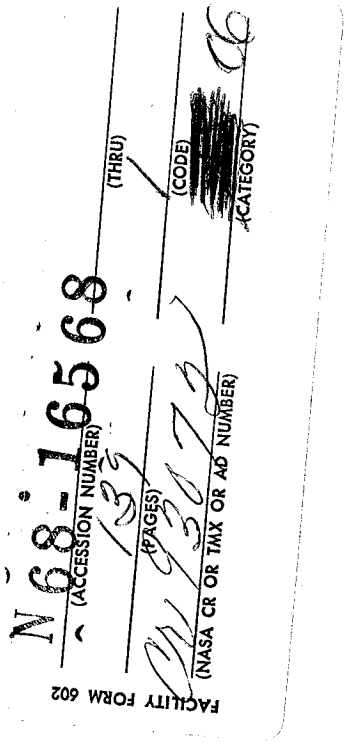
MAY 9, 1965 to MAY 8, 1966

DEVELOPMENT OF VULCANIZABLE ELASTOMERS SUITABLE FOR USE IN CONTACT WITH LIQUID OXYGEN



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DEVELOPMENT OF VULCANIZABLE ELASTOMERS SUITABLE FOR USE IN CONTACT WITH LIQUID OXYGEN

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May 9, 1965 to May 8, 1966

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FOREWORD

This report was prepared by Peninsular ChemResearch, Inc., under Contract NAS8-5352, "Development of Vulcanizable Elastomers Suitable For Use in Contact With Liquid Oxygen," with the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the technical direction of the Propulsion and Vehicle Engineering Laboratory, Materials Division of the George C. Marshall Space Flight Center with Dr. William Hill acting as the Contracting Officer's Technical Representative.

Other personnel who have contributed to this research were T. W. Brooks, D. A. Warner, Senior Research Chemists; G. Westmoreland, V. D. McGinniss, H. Meadows, Research Chemists; B. Gianinni, R. Harrell and L. Sapp, Technicians. Drs. George Butler and Paul Tarrant are acting consultants. In addition, Dr. Wallace Brey of the University of Florida supplied valuable assistance in interpretation of NMR spectra and Dr. R. J. Hanrahan, also of the University of Florida, assisted in polymerization studies.

ABSTRACT

Three members of a homologous series of fluorocarbon vinyl ethers have been prepared. Copolymerization of $CF_3OCF=CF_2$, $C_2F_5OCF=CF_2$ and $C_3F_7OCF=CF_2$ with CF_3NO, when run at high pressure, yields high molecular weight "nitroso" polymers. The T_g of these polymers ranged between -1 and -7.5°. Attempted copolymerization of $(CF_3O)_2C=CF_2$ with CF_3NO at high pressure resulted mainly in the formation of the corresponding oxazetadine and a small amount of brittle polymer. Copolymers of the three vinyl ethers with $CF_2=CH_2$ gave excellent elastomeric polymers. Terpolymers of $CF_3OCF=CF_2$, C_2H_4, C_2F_4 were prepared. Unlike the Co^{60} initiated copolymerization of $(CF_3O)_2C=CF_2$ with C_2F_4 or with $CF_2=CH_2$, it was found possible to prepare these copolymers at 1000 atm. pressure using a free radical initiator. The copolymer of $(CF_3O)_2C=CF_2$ with $CF_2=CH_2$ was found to melt at 150 to 160° and was molded into a transparent, tough film. Variable results were obtained in attempts to copolymerize CF_3CHO with C_2F_4. A single tough, thermoplastic copolymer was prepared, but waxy, brittle polymers, melting above 300°, were generally obtained. Poly-(ethylene perfluoroglutarate) was prepared but attempts to cure the polymer with a diisocyanate were not successful. CF_3OF was evaluated as a low temperature polymerization initiator.

Reaction of $CF_3OCHFCFClOCF_3$ with KOH results in dehydromethoxylation rather than the expected dehydrochlorination. Attempts to obtain $CF_2=CFC(OCF_3)=CF_2$ through pyrolysis of $\overline{CF_2CF_2CF=COCF_3}$ were not successful. An attempt to prepare $(CF_3)_2CFOCF=CF_2$ by reaction of $KOCF(CF_3)_2$ with C_2F_4 and an attempt to prepare a fluorocarbon polysulfide were not successful. A new attempt to synthesize $CF_3OCF=CFOCF$ was started. $CF_2=CFCOF$ was prepared through pyrolysis of $(CF_2)_2(COONa)_2$.

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INTRODUCTION

This report describes work carried out during the third year of Contract NAS8-5352. It is preceeded by twenty-four monthly reports, nine quarterly reports, and two annual Summary reports.

Past efforts and the ultimate goal of this project, to develop elastomeric polymer systems which are vulcanizable and suitable for use in contact with liquid oxygen, make it quite evident that the required systems will be polymeric systems containing large proportions of fluorine and/or chlorine.

Due to the lack of data concerning low temperature properties of halocarbon polymers, in particular those of the fluorocarbons, it is necessary, at least initially, to attempt to relate structural features of the hydrocarbon and available halocarbon polymer systems which enhance low temperature properties. Obviously, the desired low temperature properties which may be directly related to a polymer's usefulness at cryogenic temperature are mechanical properties. Unfortunately, a thorough search of the literature reveals little information in this area. In lieu of this information, other thermal properties which are more readily available in the literature have been chosen for comparison. These properties are the crystalline melting point (T_m) and the glass transition temperature (T_g). A correlation between T_m and T_g has been recognized[1-3] which permits an approximation of T_g from a knowledge of the more readily available T_m. Thus, for symmetrical crystalline polymers as poly(ethylene) $T_m = 2T_g$ and for unsymmetrical crystalline polymers as poly(propylene) $T_m = 1.4\ T_g$ in °K.

Unfortunately, the usefulness of this relationship is limited for the present investigation since non-crystalline polymers, such as the elastomers desired in this work, melt over a considerable range allowing the possibility of only an extremely crude, if any, approximation of T_g from the melting range. It would thus appear that any extensive correlation of polymer properties with structure without resorting to actual temperature-property-structure determination must necessarily rely on literature references to T_g data. The relationship of glass transition temperatures to mechanical properties of a polymer is not known at this point but in the

(1) R. R. Boyer, "Changements de Phases" p. 383, pub. by Soc. de Chemie Physique, Paris, 1952.

(2) R. G. Beaman, J. Polymer Sci., 9, 472(1953).

(3) E. Jenkel, Kolloid-Z., 130, 64(1953).

present investigation a good correlation between T_g and modulus of rigidity and also the Clash-Berg stiffness test has been obtained for the copolymer system, $CH_2=CF_2/CF_3OCF=CF_2$. Boyer[4] has, in addition, proposed a possible correlation between the area under the curve of transitions occuring below T_g and impact strength.

In a recent technical review by Shen and Eisenberg[5], concerned with polymer glass transition temperatures, some interesting data are presented, which further support our present view concerning the desirability of preparing fluorocarbon vinyl ethers having increased side chain length. By systematically increasing the chain length of a alkyl group in poly(alkyl methacrylates) ($R=CH_3$, T_g 100°; $R=C_{18}H_{37}$, T_g -100°) T_g is reduced 200°. Somewhat surprising also is the lowering of T_g of poly(styrene) from 105° to -65° by increasing the chain length of a p-alkyl group to C_{10}. This is a decrease in T_g of 170°. These low values were terminal values on a plot of a homolgous series and did not represent minima. This would indicate that no side chain crystallization is occurring as observed by Lal and Trick[6] for a series of vinyl ethers which exhibited a minimum T_g at $R=C_8$.

In effect, the side chain is acting as a chemically bonded plasticizer. The effect of this type of plasticization on physical properties of the polymers below T_g is of particular interest in the present study.

Additional discussion concerning the effect of polymer structure on the glass transition temperature is included in the First and Second Annual Reports.

(4) R. F. Boyer, Rubber Chem. and Tech., 36(5), 1303-1421(1963).

(5) M. C. Shen and Adi Eisenberg, NONR 233(87) Tech. Rpt. No. 9, August 1, 1965.

(6) J. Lal and G. Trick, J. Polymer Sci., Pt. A, 2(10) 4559-72(1964).

DISCUSSION

A. Polymers

1. $(CF_3O)_2C=CF_2$(PVM) Copolymers

Due to the difficulty in obtaining any sizeable quantities of PVM, evaluation of this monomer has been limited to a few copolymers.

Attempts to prepare C_2F_4(TFE)/PVM copolymers through irradiation at room temperature at autogenous pressures resulted in little, if any, copolymerization. The polymers obtained were brittle, waxy solids resembling low molecular weight poly(TFE). The PVM appears to be only stopping the chain growth with little actually being incorporated into the polymer. In contrast to this, attempts to copolymerize PVM with $CF_2=CH_2$(VF_2), using Co^{60} initiation, have resulted in high conversions to polymer, but the polymer is infusible and in all probability cross-linked.

Irradiation of PVM/VF_2 in which the dose rate was reduced to less than half that of previous samples (Table IV, 203 and 209) resulted in a lower conversion to polymer but again yielded a copolymer which appeared to be cross-linked. When heated under pressure the polymer did not fuse into a continuous film.

In order to prepare copolymers of PVM which would be useful for evaluation purposes it was necessary to carry out a radical initiated polymerization at about 1000 atmospheres pressure. In this way a copolymer of PVM/TFE was prepared (Table II, Exp. 12P) which was shown by analysis of the residual overgas and elemental analysis of the polymer to contain 15 mole % of PVM. It could be molded into a tough, transparent film at 314°. The infrared spectrum of the film was not substantially different from that of poly(TFE), probably because of the low concentration of combined PVM. As further evidence of copolymerization the molding characteristics and film clarity were quite unlike that of a homopolymer of TFE.

An unfortunate characteristic of TFE monomer at high pressures restricts, to some degree, the use of TFE as a comonomer. An attempt to evaluate the high pressure polymerization apparatus, a homopolymerization of TFE, using asobis-isobutyronitrile as the initiator, resulted in almost a quantitative conversion of the monomer to CF_4 and carbon. During the warm-up period the violent reaction and accompanying exotherm caused a pressure surge from 18,000 to an estimated 40,000 psi. Only 2.4 g. of TFE was used in this polymerization attempt.

Copolymerization of equimolar amounts of TFE with other comonomers in general yielded polymers which did not decompose during polymerization. On one occassion (Table II, Exp. 35) copolymerization of $C_2F_5OCF=CF_2$ (EVE) with $CF_2=CH_2$ (VF_2) resulted in carbonization. This was the only time this occurred using VF_2 as the comonomer.

Copolymerization of PVM with VF_2 (Table II, Exp. 33) at 1000 atm. pressure yielded a thermoplastic polymer which had a fairly sharp melting point at 150-160°. This would indicate a fair degree of crystallinity which suggests the possibility of estimating T_g for this copolymer from the $T_g = T_m/2$ relationship. In this way a T_g is found to be -57 to -62°. Since T_g for poly (VF_2) is -45° these values tend to support our previous estimate of -60° as the T_g of a homopolymer of PVM.

2. $\underline{CF_3OCF=CF_2}$ (MVE) Copolymers

a. $\underline{C_2F_4}$ (TFE)/MVE

In our present effort to evaluate the effect of side chain length on the low temperature properties of the poly(perfluoroalkyl vinyl ethers) a number of MVE/TFE copolymers were prepared (Tables II and IV). These samples, ranging from 12.5 to 68 mole % MVE, were thermoplastic and molded easily to give clear, tough flexible films. Qualitatively, the films appear to become increasingly more elastic when the MVE content is increased.

Two copolymer samples of MVE/TFE were submitted to the Materials Division for a preliminary evaluation of physical properties below T_g. These samples, 223 (containing 34.6 wt. % MVE) and 235-9 (containing 44.6 wt. % MVE), represent the first in a homologous series of fluorocarbon vinyl ethers which will be prepared in an attempt to determine the effect of pendent chain length on physical properties below T_g.

Sample 223 was qualitatively examined by flexing while submerged in liquid N_2(-196°). It was found possible to bend the film (about 0.02" thick) to about a 1/2" radius without fracturing.

The quantity of sample thus far submitted to the Materials Division is not sufficient for any extensive testing, but should be sufficient for a single series of tests at an arbitrarily selected test temperature of -80°. It should be possible to obtain some values for residual mechanical properties below T_g, values which at present are unknown. A comparison of these values with that of Teflon would be of particular interest and the tensile strength and elongation of Teflon at -80° may serve as a standard for future comparisons.

It is interesting to note than an increase from 34.7 to 44.6 wt. % MVE in the copolymer decreased the molding temperature about 150° and apparently decreased the thermal stability also, since attempts to mold 235-9 at 150° and above resulted in the formation of numerous bubbles in the film. This decomposition may be related to the difficulty encountered in our attempts to prepare $CF_2=CFC(OCF_3)=CF_2$ by the pyrolysis of $CF_2CF_2CF=COCF_3$.

b. TFE/C_2H_4/MVE

In an attempt to further broaden our knowledge concerning the relation of low temperature polymer properties to structure, it was considered of interest to determine the effect of a termonomer on T_g. Of particular interest would be a third monomer randomly placed along the polymer chain which might impart added flexibility. Although T_g of copolymers depends on the copolymer composition according to a weighted average of the two homopolymers, it is conceivable that a third monomer, of small bulk, might have a greater effect than a weighted average might predict.

In an initial attempt to prepare this terpolymer, using Co^{60} initiation, polymerization occurred at about the same rate as comparable MVE/TFE copolymerizations. Although these initial samples did not mold well, small clear portions indicated an improvement in extensibility over than of comparable MVE/TFE copolymers. An additional attempt (248-50 Table IV) on a larger scale, at a reduced irradiation dose, resulted in essentially the same inhomogeneous polymer. The inhomogeneity was again noted when attempting to mold the polymer. When heated to 320° at 6000 psi the polymer flowed easily, but when cooled under pressure the resultant film had a cloudy, mottled appearance and contained numerous cracks. This inhomogeneity is probably due to a combination of a change in polymer composition with time during the irradiation period and to some degree of cross-linking.

A subsequent attempt to prepare the terpolymer at 1000 atm. pressure using an azo initiator (Table II, 19P), resulted in violent decomposition. As indicated earlier, this decomposition is presumed to be due to the high concentration of TFE present.

3. $C_2F_5OCF=CF_2$(EVE) and $C_3F_7OCF=CF_2$(PVE) Copolymers

Several copolymers of EVE and PVE with VF_2 have been prepared (Table II, Exp. 35, 36, 40 and 45). The high pressure, bulk polymerization of VF_2/EVE, using a monomer ratio of 3.3/1, gave a high yield of an excellent, tough elastomer. The copolymer contained 43 wt. % EVE and the T_g, as measured by a viscous flow apparatus, was found to lie between -25 and -20°. (See note, Table III).

Two copolymers of EVE/TFE were prepared using a 1/3 and a 1/4 molar ratio of monomers. Similar to the Co^{60} initiation of MVE/TFE copolymers, a short radiation time gave essentially 100% conversion to polymer. However, unlike the MVE/TFE copolymers, these copolymers appeared inhomogeneous when molded into film.

The high pressure, bulk polymerization of VF_2/PVE, using a 3/1 monomer ratio, yielded a tough elastomeric polymer containing an average of about 7 mole % PVE. This polymerization was unusual in that the polymer composition varied between 4 mole % PVE in the lower part and 10% in the upper part of the polymerization tube. The upper portion was noticeably more elastomeric than the lower portion.

The T_g of the copolymer containing 30.5 wt. % PVE (Table III, 45P-1) was found to be about -31°.

The T_g of homopolymers of EVE and PVE were estimated by a rough plot of T_g vs copolymer composition, taking T_g of poly(VF_2) as -45°. If the values obtained (-10 to +2°) are approximately correct, it would appear that T_g is nearly independent of the length of the alkoxy side chain, since the T_g of poly(MVE) (-5°) also lies in this range. Additional data will be required to verify this observation.

4. $R_fOCF=CF_2/CF_3NO$ Copolymers

A number of earlier attempts[7] to copolymerize MVE with CF_3NO using conventional nitroso polymerization techniques (autogenous pressure at low temperatures) yielded a mixture of a low molecular weight polymer oil and the cyclic "dimer" $CF_3\overline{NCF_2CF(OCF_3)O}$.

In a reinvestigation of this copolymer system it was found that a fair yield of high molecular weight polymer could be obtained if the polymerization was carried out at high pressure. It is interesting to note that the pressure at which polymerization may be carried out is limited to about 700 or 800 atm. This limitation was noted in the first attempt to copolymerize MVE with CF_3NO. During pressurization of the monomer mixture a sudden pressure surge occurred, starting at about 810 to 950 atm., the pressure rose to 1,200 atm. (Table II, Exp. 1P). This surge in pressure opened the end seal in the reactor tube and the monomer was lost. It appeared from this that a critical pressure was attained, in the vicinity of 800 to 900 atm. At this pressure a highly exothermic reaction occurred causing the observed rise in pressure. Any polymer which might have formed apparently decomposed since only a trace amount was found in the reaction tube.

(7) First Annual Report, this contract.

It was found that by carrying out the polymerization at 0° and by not exceeding this apparent "critical pressure," fair yields of high molecular weight "nitroso" polymers containing pendent perfluoroalkoxy groups could be prepared. Typical infrared spectra of the MVE, EVE and PVE "nitroso" polymers are shown in Figures 1, 2, and 3.

One exception to this improved polymer yield and molecular weight was found when attempts were made to copolymerize PVM with CF_3NO. When the reaction was run either at room temperature and 1000 atm. pressure, or at 430-680 atm. and 0°, only a small amount of a brittle polymer was obtained. The bulk of the monomers was converted to the cyclic "dimer", perfluoro(2-methyl-4,4-dimethoxy-1,2-oxazetadine). An infrared spectrum of this compound, and that of the oxazetadines obtained as by-products in other "nitroso" polymer preparations, are shown in Figures 4, 5 and 6.

The glass transition temperature of the first member in this series of "nitroso" polymers (MVE/CF_3NO, Table I), determined by DTA, was found to be -5°. A similar value, -1°, was obtained using a viscous flow apparatus (see note, Table III). The other members in this series have essentially the same T_g, ranging between -7.5 to -1°.

It is interesting to compare the T_g of these polymers with that of vinyl polymers having the same pendent groups. Poly(C_3F_6), having pendent CF_3 groups, has a T_g of +165°. By replacing this CF_3 with a pendent OCF_3 group, as in poly(MVE), T_g is decreased 170°. In contrast to this the T_g of "nitroso" polymers having the structure

$$-\left(-N(CF_3)-O-CF(R_f)-CF_2-\right)-$$

changes little, if any, when R_f is $-CF_3$ or $-OR_f'$. Since T_g is in essence the point at which immobilization of the polymer backbone occurs, apparently the close proximity of the two pendent groups on the polymer chain restricts rotation and in turn reduces the flexibility of the $-N-O-C-C-$ polymer backbone. Little added restriction occurs when the alkoxy chain length is increased to $-OC_3F_7$. However, an increase in T_g is noted when a second OCF_3 group is added, as with $CF_3NO/(CF_3O)_2C=CF_2$ copolymers, where the backbone flexibility is further reduced resulting in a polymer which is hard and brittle at room temperature. Stewart and Breigleb models of these copolymers show added restriction to rotation over that of the usual CF_3NO/C_2F_4 copolymer.

This observation takes on special significance when we consider our concurrent objective on this program, the preparation of polymers containing heteroatoms in the polymer backbone.

TABLE I

T_g of Some Nitroso Polymers[a]

R_fNO	Olefin	T_g
CF_3	C_2F_4	-51°
CF_3	C_3F_6	-9°
CF_3	$CF_2=CFCH=CH_2$	-55°
CF_3	$CF_3OCF=CF_2$	-5°, -1°
CF_3	$C_2F_5OCF=CF_2$	-2.5°, -7.5°
CF_3	$C_3F_7OCF=CF_2$	-1°, -1.5°
CF_3	$(CF_3O)_2C=CF_2$	brittle at RT
C_2F_5	C_2F_4	-51°
C_3F_7	C_2F_4	-32°
C_8F_{17}	C_2F_4	-25°
CF_2ClCF_2	C_2F_4	-48°
$NO_2CF_2CF_2$	C_2F_4	-41°

(a) T_g of vinyl ether copolymers determined on viscous flow apparatus (see Note, Table III). Remaining values compiled from T_g data (determined by refractive index) in Minnesota Mining and Mfg. reports on Contract No. DA-19-129-QM-1043(1960-61).

similar in appearance to Exp. 255 but were considerably weaker. The copolymer containing 40 mole % TAA would not mold at 330° (temperature limit of press) but when crudely pressed in a test tube over a direct flame the polymer fused into a rough, opaque pellet. Unlike Exp. 255, infrared spectra of these polymers were very much like that of poly(TFE).

6. $CF_2=CFCH=CH_2$ (TB)

In reviewing early polymer work carried out under the Arctic Rubber Program[10], it was noted that copolymers of $CF_2=CFCH=CF_2$ and $CF_2=CHCF=CH_2$ with olefins such as $CF_2=CCl_2$ had Gehman T_{100} temperatures of lower than -50°. (Gehman T_{100} appears to be roughly comparable to the glass transition temperature of a polymer.) An estimate of T_g for the homopolymer of $CF_2=CCl_2$[11] of +50° suggested a low T_g for these butadienes (-60 to -70°).[2] Since some future work will be concerned with trifluoromethoxy-substituted butadienes, it was considered of interest to determine T_g for poly(TB). A small amount of this polymer was prepared, using an emulsion recipe, and thermal analysis indicated a T_g of -37° (Table VI). This is somewhat higher than predicted above.

Attempts to copolymerize TB with MVE using γ-ray initiation at room temperature resulted in homopolymerization of TB(Table IV, Exp. 226 - 229). This diene homopolymerizes very rapidly and is known to polymerize explosively; therefore, the exclusion of the much more difficultly polymerizable vinyl ether is not unexpected. However, copolymerization of an approximately equimolar mixture of the butadiene with $CF_3OCF=CF_2$ at about 1000 atm. pressure, using azobis-isobutyronitrile initiator, gave a copolymer containing 3 to 8% of the vinyl ether. Unfortunately, this polymer was extremely tough and could not be molded into a homogeneous film.

7. Poly(ethylene perfluoroglutarate)

In an attempt to prepare a readily curable elastomer with good liquid oxygen compatability, poly(ethylene perfluoroglutarate) was synthesized and subjected to a conventional polyurethane curing process.[12] The polyester had a molecular weight of 4,500 which corresponds to a $\overline{DP}$ of 17.

(10) U. S. Army Contract No. DA-44-109 ghr-222, Report No. RL-54-333, 7/50 to 7/53.

(11) Table I in Second Annual Report, this contract.

(12) A. Pigott, B. F. Frye, K. R. Allen, S. Steingiser, W. C. Dorr, and J. H. Saunders, J. Chem. Eng. Data, 5, 391(1960).

Molecular weight had to be determined by vapor pressure osmometry because the polyester was too hydrolytically unstable to be analyzed by the usual end group titration methods. (The hydrolytic instability of fluorocarbon esters is discussed further under Part B.)

Attempts to extend and cure the polyester using toluene-2,4-diisocyanate and 1,4-butanediol led to some chain extension, as evidenced by an increase in melt viscosity, but failed to afford a cured elastomer. The products were always white, sticky gums.

8. $CF_3C{\equiv}CCF_3$ and Copolymers

The polymerization of this monomer was studied on a limited basis to determine if the intractable nature of this polymer may be modified sufficiently, through copolymerization, to yield a useful polymer. This is an interesting monomer which reportedly[13] undergoes polymerization quite readily to give a polymer which is infusible and insoluble. The ease with which polymerization occurs is supported by our own work as shown in Table IV.

The intractable nature of this polymer is probably due to its ladder-type structure. Our first attempts to modify this structure, to break up the regularity in the chain, were through copolymerization with $CF_2{=}CFCF{=}CF_2$ and $CF_3OCF{=}CF_2$. The polymer obtained with the vinyl ether appears to have properties very much like that of the homopolymer of the butyne but the reduced rate of polymerization would indicate that some vinyl ether had reacted. The attempted copolymerization with the diene is somewhat more encouraging in that a trace amount of tacky liquid was obtained.

9. CF_3COCF_3(HFA)/TFE

In some recent papers by Krespan[14] and by Engelhart[15] the copolymerization of fluorocarbon ketones was shown to occur to give polymers containing oxygen in the polymer chain. Although other routes to fluorocarbon polyethers are available, thus far no high molecular weight polymers have been obtained. Little is said by either author concerning molecular

(13) H. C. Brown and H. Gewanter, J. Org. Chem., 25, 2071-2(1960).

(14) C. Krespan, Seminar at University of Florida, 5 Feb. 1965.

(15) V. A. Engelhardt, 3rd International Symposium of Fluorine Chemistry, Munich, Germany; also Chem. and Eng. News, 43(41), 80(1965).

weight or properties of these polyethers but copolymerization of TFE with hexafluoroacetone (HFA) was mentioned.

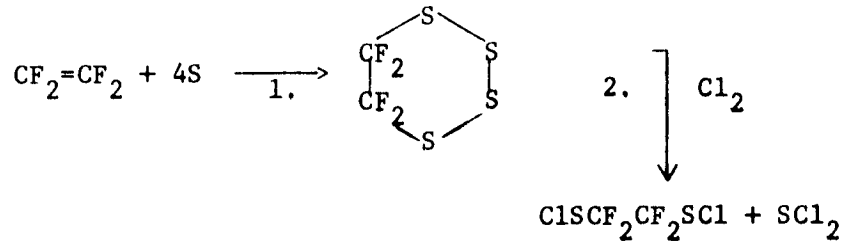
This method of introducing a heteroatom into a fluorocarbon polymer chain appears quite attractive. Judging by the low glass transition temperature of poly(thiocarbonyl fluoride)[15] of -118°, the T_g of a copolymer of HFA and TFE should be quite low.

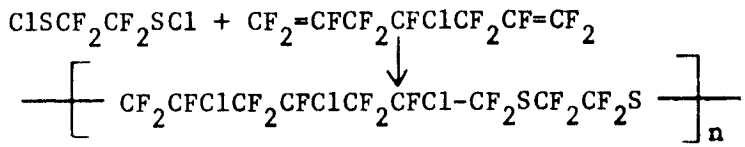
A preliminary attempt was made to copolymerize TFE/HFA and $CF_3OCF=CF_2$/HFA. Irradiation of approximately equimolar amounts of TFE/HFA gave a fairly high yield of a waxy polymer which molded into a brittle, waxy film. The character of this polymer is quite similar to low molecular weight poly(tetrafluoroethylene) obtained through thermal degradation of Teflon. The MVE/HEP copolymerization attempt resulted in only a trace of tacky oil.

It would appear that in both of these experiments very little, if any, HFA copolymerized. With C_2F_4 the HFA probably copolymerized to the extent of limiting chain growth since C_2F_4 under similar conditions would have yielded a high molecular weight, tough polymer.

10. Attempted Preparation of a Fluorocarbon Polysulfide

The following reaction sequence was carried out in an experiment to determine the feasibility of preparing a polymer containing a heteroatom, sulfur, in the polymer chain.





The perfluoro-1,2,3,4-tetrathiane and the perfluoro-1,2-bis sulfenyl chloride were prepared by using Krespan's[16] method. The NMR

(16) C. G. Krespan, U. S. Pat. 3,099,688.

analysis of the disulfenyl chloride indicated only one material present but elemental analysis was high for sulfur and chlorine and low for carbon and fluorine. This would suggest contamination with SCl_2 which would not be detected by NMR.

When an equimolar mixture of the disulfenyl chloride and the diolefine, shown above, was exposed to sunlight for a two week period, no apparent reaction occurred.

11. CF_3OF as a Low Temperature Polymerization Initiator

A simple attempt was made to initiate polymerization of C_2F_4 with CF_3OF. A trace amount of CF_3OF was combined with F_2F_4 in a Pyrex ampule at -196° and the reaction mixture was allowed to warm to room temperature. Immediately on warming, a small amount of polymer was noted on the walls of the ampule. The polymerization appeared to terminate early since no additional polymer formed after an extended time at room temperature.

A second attempt was made to telomerize CF_2=CFCl with CF_3OF. This reaction was run in a Freon 113 solvent system. Once again only a trace of product was found. This reaction gave a trace amount of high boiling liquid.

B. Synthesis

1. PVM

Due to the difficulties in preparing this monomer only a limited amount of effort has been expended in its synthesis during this period.

A review of the steps in this synthesis will serve to indicate the difficulties encountered.

1. $CF_3OF + CHCl{=}CCL_2 \longrightarrow CF_3OCHClCFCl_2$ (58.6%)

+

CF_3OCCl_2CHFCl (3.2%)

2. $CF_3OCHClCFCl_2 \xrightarrow[DMSO]{Zn} CF_3OCH{=}CFCl$ (cis and trans) 90.5%

3. $CF_3OF + CF_3OCH{=}CFCl \longrightarrow (CF_3O)_2CHCF_2Cl$ (22.4%)

\+ (isomer ratio 71/29)

$CF_3OCHFCFClOCF_3$

4. $(CF_3O)_2CHCF_2Cl \xrightarrow[Nujol]{KOH} (CF_3O)_2C{=}CF_2$ (34.6%)

An overall yield, based on $CHCl{=}CCl_2$ used, may be calculated as 4.1%.

An accompanying difficulty was found in attempts to separate the geometric isomers in step 3. The purest 1,1 adduct obtained thus far, through distillation, has been a 90/10 mixture of the two isomers. As a consequence of this, step 4 invariably contains both isomers and the dehydrochlorination yields varying amounts of $(CF_3O)_2C{=}CF_2$. Distillation of the dehydrochlorination products, with the major portion of the distillate boiling at 13°, gives a product containing 78% PVM, 12% of a mixture (single GLC peak) of $CF_3OCF{=}CFCl$ and $CF_3OCCl{=}CF_2$ (see discussion below) and, surprisingly, 6.8% of cis and trans $CF_3OCH{=}CFCl$.

In order to facilitate study of PVM polymers an attempt was made to copolymerize PVM as distilled to determine if the olefinic impurities present would inhibit polymerization. The polymerization was carried out using conditions which previously gave high conversions to polymer with GLC pure PVM. In Table IV, Experiment No. 203A summarizes the results of this attempt. The resultant polymer was a high viscosity liquid or tacky gum of obviously low molecular weight. The conversion of 47% and conversion rate of 1.0%/hr. may be compared with a previous polymerization, which was carried out using GLC pure PVM, where an 80.6% conversion and a rate of 1.7%/hr. was obtained. It is obvious that the impurities present in the distilled PVM cause inhibition. The results of an attempt to copolymerize $CF_3OCH{=}CFCl$ confirm this, since only low conversions to low molecular weight polymer were obtained (Table IV). It is thus necessary to carry out the final purification by GLC.

In the preparation and characterization of PVM frequent reference has been made to the presence of the isomeric olefin $CF_3OCF{=}CFOCF_3$.

The precursor to this compound, which has been shown by NMR analysis (see Experimental) to be $CF_3OCHFCFClOCF_3$, is not completely separated from crude $(CF_3O)_2CHCF_2Cl$ by distillation. Therefore, it was reasonable to expect that the two isomeric olefins should be formed on dehydrochlorination. Gas chromatographic analysis of the olefinic product did indeed show two peaks. The larger one has been firmly identified as PVM. The smaller peak has been shown by vapor density molecular weight (182-187), and NMR analysis to be a three component mixture: $CF_3OCCl=CF_2$, 30%; cis-$CF_3OCF=CFCl$, 59%; and trans-$CF_3OCF=CFCl$, 11%. Attempts to resolve this mixture on a variety of GLC columns were unsuccessful.

The results of the NMR analysis are summarized below with chemical shifts for fluorine given with respect to external CF_3COOH.

$CF_3OCCl=CF_2$ (A)

Chemical Shift ppm	Pattern and Splitting cps	Rel. Area	Assignment
-15.5	2° x 4.51	4.7	CF_3O
+28.8	2° x 48.7, 4° x 4.3	1.6	=CF
+45.2	2° x 49.8	1.7	=CF

(cis)$CF_3OCF=CFCl$ (B)

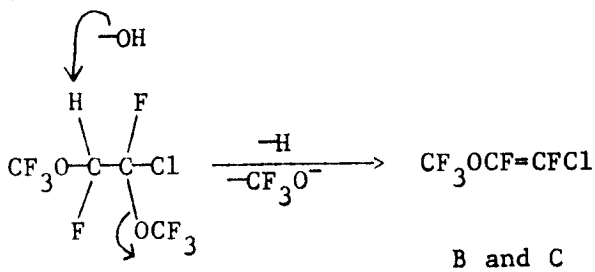
-14.6	2° x 4.3	9.2	CF_3O
+17.0	2° x 42.4, 4° x 4.4	3.1	=CF
+26.1	2° x 43.2	2.9	=CF

(trans)$CF_3OCF=CFCl$ (C)

-15.2	3° x 4.2	1.8	CF_3O
+44.4	2° x 120, 4° x 4.3	0.8	=CF
+51.8	2° x 120, 4° x 4.3	0.9	=CF

The results of this analysis would suggest that in the dehydrohalogenation step the 1,2 isomer preferentially eliminates a trifluoromethoxy

group. Thus, the following mechanism would account for the presence of cis and trans $CF_3OCF{=}CFCl$.



B and C

However, on the same mechanistic basis it is somewhat more difficult to rationalize the presence of (A). It is conceivable that (A) might arise, in a similar way, from the dehydromethoxylation of $(CF_3O)_2CClCF_2H$, but the presence of anything but a trace amount of this compound would appear unlikely. This is evident when reviewing the overall reaction sequence shown earlier. Although it would be interesting to determine the actual source of compound (A), little practical benefit would be gained from this information.

The unexpected result of this reaction does not adversely affect the preparation of PVM but it does, at least for the present, prevent evaluation of $CF_3OCF{=}CFOCF_3$ as a monomer.

2. Attempted Alternate Synthesis of PVM

The difficulty in preparing PVM, as discussed above, has hampered our evaluation of this monomer. It was considered advisable to investigate, at least to a limited extent, alternate preparative methods. One such possibility is through the following reaction sequence.

$$2CF_3OF + HC{\equiv}CCOOH \longrightarrow (CF_3O)_2CHCF_2COOH$$

$$(CF_3O)_2CHCF_2COOH \xrightarrow[2.\ I_2,\Delta]{1.\ Ag_2O} (CF_3O)_2CHCF_2I$$

$$(CF_3O)_2CHCF_2I \xrightarrow{KOH} (CF_3O)_2C{=}CF_2$$

Unfortunately, the first reaction does not occur as shown. Reaction of CF_3OF with the propiolic acid results in a solid product and recovery of almost all of the original CF_3OF. An infrared spectrum of the solid shows two broad maxima at about 3 and 5.8μ indicating a carboxyl group and no

triple bond absorption at 4.7μ. This material was not further investigated since it was obvious that the desired reaction did not occur.

By analogy to the reaction of SF_5OF with CF_2=CFCOF in which O-F addition to the double bond occurs readily, a second approach was attempted in which CF_3OF was reacted with propiolyl chloride (HC≡CCOCl). Initially it appeared that the triple bond was quite unreactive; the reactivity of the propiolyl chloride appeared to be about the same as propiolic acid. However, when the acid chloride and CF_3OF were reacted at low pressure, a trace amount of product was obtained which exhibited an infrared absorption maximum at 5.57μ. This absorption maximum is consistent with a $-CF_2COCl$ carbonyl absorption.

Other attempts at this reaction met with similar results. One of these reactions, however, served to demonstrate the unpredictable reactivity of CF_3OF. A small amount of CF_3OF was added to a Pyrex reactor containing HC≡CCOCl. No apparent reaction occurred, as indicated by the pressure in the reactor, and a second addition of CF_3OF was made. Again no reaction appeared to occur and the pressure in the reactor increased with the second addition. While being cooled in liquid N_2 the mixture exploded. The explosion appeared to occur in the vapor state since the upper portion of the protective screen was expanded while the lower portion was not. Investigation of this reaction was discontinued.

3. Attempted Synthesis of CF_3OCF=$CFOCF_3$

As shown in the preparation of PVM, the reaction of $CF_3OCHFCFClOCF_3$ with KOH resulted in dehydromethoxylation rather than the expected dehydrochlorination.

A new synthetic route was devised specifically for the preparation of CF_3OCF=$CFOCF_3$.

1. $CF_3OF + CCl_2$=$CCl_2 \xrightarrow{52.8\%} CF_3OCCl_2CFCl_2$

2. $CF_3OCCL_2CFCl_2 \xrightarrow[Zn,\ Dioxane]{\sim 72\%} CF_3OCCl$=$CFCl$

3. $CF_3OF + CF_3OCCl$=$CFCl \xrightarrow{\sim 79\%} CF_3OCFClCFClOCF_3 + (CF_3O)_2CClCF_2Cl$ isomer ratio 72/28

4. $CF_3OCFClCFClOCF_3 \xrightarrow{Zn} CF_3OCF$=$CFOCF_3$

In this synthesis it was considered probable that a final dehalogenation rather than a dehydrochlorination step might be effected without loss of a trifluoromethoxy group.

Thus far this synthesis has been carried out to the third step and the desired 1,2 adduct obtained in about a 22% overall yield.

It is interesting to compare the isomer ratio of the 1,1 and 1,2 adduct in this synthesis with the equivalent step in the synthesis of PVM. The similar but reverse isomer ratios

$$CF_3OF + CF_3OCH{=}CFCl \longrightarrow \begin{matrix} (CF_3O)_2CHCF_2Cl & 71 \\ + & \\ CF_3OCFHCFClOCF_3 & 29 \end{matrix}$$

$$CF_3OF + CF_3OCCl{=}CFCl \longrightarrow \begin{matrix} (CF_3O)_2CClCF_2Cl & 28 \\ + & \\ CF_3OCFClCFClOCF_3 & 72 \end{matrix}$$

would indicate an equivalent intermediate radical stability for $CF_3O\dot{C}Cl$ and $F\dot{C}Cl$.

4. Preparation of Perfluoro(alkyl vinyl ethers)

Initial attempts to prepare the fluorocarbon vinyl ethers required in the present study met with only limited success. Low yields of the intermediate perfluoro(alkoxy-substituted propionyl fluorides) were obtained. The patent reference to this reaction[17] indicates that catalytic amounts of

1. $R_fCOF + CF_3\overline{CFCF_2O} \xrightarrow[\text{or Act.C}]{\text{CsF in diglyme}} R_fCF_2OCF(CF_3)COF$

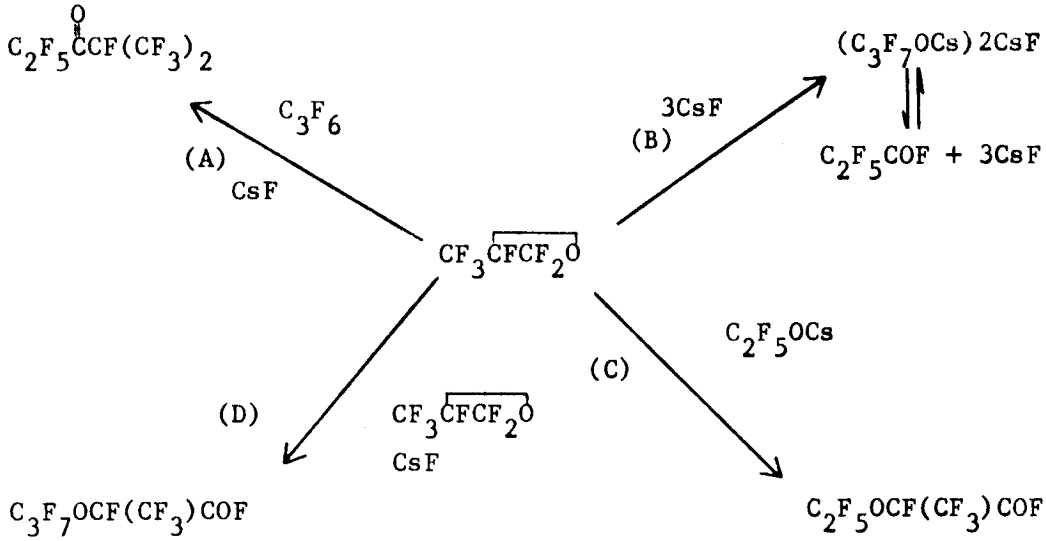
2. $R_fCF_2OCF(CF_3)COF \xrightarrow[2.\ \Delta]{1.\ NaOH} R_fCF_2OCF{=}CF_2$

either activated carbon or CsF are sufficient for good conversions to adduct. In a number of attempts (Table VIII) using catalytic amounts of carbon or CsF in diglyme invariably only low conversions to the alkoxy-substituted acid fluoride were obtained. Since these intermediates are important in

(17) C. G. Fritz, E. P. Moore, Jr., and S. Selman, U.S. Pat. 3,114,778, 17 Dec. 1963.

this study it was considered necessary to obtain additional information concerning the mechanism of this reaction.

The following reactions summarize the data obtained thus far.



The extent of reaction in each instance depends on reactant concentrations.

In our attempts to elucidate this reaction all these products were separated and identified with the exception of the cesium salts. The presence of the salt was deduced from reaction of CsF with CF_3COF in diglyme, which indicated the formation of a salt-complex in the molar ratio of 3CsF to $1CF_3COF$. This salt reacted exothermically with $CF_3\overline{CFCF_2O}$ to give good yields of $C_2F_5OCF(CF_3)COF$. Chromatographic analysis of this product showed one main product peak. However, an infrared spectrum of this peak revealed the presence of an additional material which had a carbonyl absorption at 5.6μ. The major peak was further resolved into two peaks using a longer GLC column, the minor peak (9%) was identified by infrared analysis as $CF_3\ COCF(CF_3)_2$, and the major peak (81%) as $C_2F_5OCF(CF_3)COF$. This by-product ketone is the result of reaction of the acid fluoride with C_3F_6 which was present as an impurity in the propylene oxide.[18]

(18) F. S. Fawcett and R. D. Smith, U. S. Pat. 3,185,734, 25 May 1965.

The order of addition of reactants is quite important since the propylene oxide rearranges rapidly in the presence of CsF to give C_2F_5COF. This would indicate several possible reaction routes if both the acid fluoride and propylene oxide are present. Hence, in order to obtain good yields of the desired adduct, an excess of CsF is first reacted with the acid fluoride; then addition of propylene oxide gives mainly one product.

The very low yields previously obtained, using catalytic amounts of CsF, were probably due to a second salt formation as shown,

$$R_fCOF + CF_3\overline{CFCF_2O} \xrightarrow{CsF} R_fCF_2OCF(CF_3)CF_2OCs$$

which prevented the initiation of any further reaction. This would appear to be substantiated by the fact that the yield did not increase with time.

It is interesting to note that there was no evidence of further addition occurring to give oligomers of the propylene oxide. However, small amounts may have been produced since it would be difficult to detect or isolate these higher boiling materials from the diglyme.

A recent paper by Sianesi,[19] in which the preparation of polyethers is described, suggested the possibility of preparing the desired alkoxy-substituted acid fluorides by the direct combination of O_2, $CF_3CF=CF_2$ and an acid fluoride. In the ultraviolet induced oxidation of perfluoropropene a variety of products is obtained including COF_2, CF_3COF, C_2F_5COF, $CF_3\overline{CFCF_2O}$ and a high molecular weight liquid. The product distribution varied according to conditions used, with high molecular weight products favored when the reaction was carried out in the liquid phase.

In an attempt to utilize this reaction for the preparation of the desired alkoxy-substituted acid fluorides, the oxidation of perfluoropropylene with oxygen was carried out in the presence of a fluorocarbon acid fluoride. Since perfluoropropylene oxide was found as a reaction product of $CF_3CF=CF_2$ and O_2, it was considered probable that the presence of an acid fluoride might divert the "normal" polymerization reaction to give the desired alkoxy acid fluoride [$R_fCF_2OCF(CF_3)COF$].

Several attempts were made using both u.v. and gamma ray initiation. It was found that, regardless of the mode of initiation, the predominant product was a high boiling liquid. Infrared analysis gave no indication of the simple adduct. Although these reactions did not proceed as desired, it is interesting to note that the two means of initiation gave what appear to be two different high molecular weight products. The high boiling products are

(19) D. Sianesi, A. Pasetti and C. Corti, Makro. Chemie, 86, 308-11(1965).

obviously a mixture of compounds, but when u.v. initiation was used the high boiling reaction product of $C_3F_6/O_2/CF_3COF$ showed a carbonyl absorption at 5.25μ (as reported by Sianesi[19]). On the other hand, when $C_3F_6/O_2/C_3F_7COF$ was irradiated with gamma rays, the carbonyl absorption of the high molecular weight product was found at 5.30μ.

The carbonyl absorption of the latter product is consistent with that of a fluorocarbon acid fluoride and Moore, et al.[20] also report a carbonyl absorption at 5.3μ for oligomers of perfluoropropylene epoxide.

$$C_3F_7\ [\ OCF(CF_3)CF_2O\ ]_xCF(CF_3)COF$$

The carbonyl absorption at 5.25μ for polymers formed by photo-oxidation of C_3F_6 might possibly be due to OCOF termination since Sianesi found that u.v. irradiation of equimolar mixtures of C_3F_6 and O_2 gave a liquid polymer which analyzed as $(CF_2O)_x$. Termination in this instance could give rise to the OCOF group as shown below:

$$CF_2OCF_2O\cdot \xrightarrow{-F\cdot} CF_2OCOF$$

5. Preparation of CF_2=CFOSF_5

As discussed at length in the Second Annual Report the only successful method found thus far for the preparation of $SF_5OCF=CF_2$ has been through dehydrobromination of $SF_5OCFBrCF_2H$. Unfortunately, this material is only available as a minor product in the reaction of SF_5OF with CHF=CFBr.

The limited availability of this minor isomer has hampered efforts to prepare and evaluate polymers of $SF_5OCF=CF_2$. An additional difficulty was encountered when an attempt was made to dehydrobrominate 3 g. of pure $SF_5OCFBrCHF_2$. Reaction of the adduct with KOH in a closed system resulted in a low conversion to the unsaturated compound. Repeated passes over hot KOH (to 100°) appeared to cause decomposition since a loss of product was noted after successive passes. Unlike decomposition of $SF_5OCHFCF_2Br$ with KOH, however, a qualitative test of the KOH residue, after reaction of the $SF_5OCFBrCHF_2$, was negative for $SO_4^=$.

In view of the difficulty encountered in the preparation of this monomer and the probable limited contribution toward an overall study of structure vs low temperature properties of polymers, it would seem wise to devote less time toward this synthesis and concentrate efforts on more

(20) E. P. Moore, A. S. Milian and H. Eleuterio, Fr. Pat. 1,275,799, Oct. 2, 1961.

promising areas outlined previously. However, two additional approaches to the preparation of this monomer were attempted during this period as a final effort in this synthesis.

In the first approach it appeared advisable to continue with the only successful method devised thus far, i.e. dehydrohalogenation of $SF_5OCHFCF_2Cl$. In the addition of SF_5OF to CHF=CFCl it was expected that the isomer ratio would be more favorable than that of the corresponding addition to CHF=CFBr.

Several grams of the SF_5OF/CHF=CFCl addition product was prepared but contrary to expectations the isomer ratio (as indicated by GLC analysis) was considerably lower ($SF_5OCFClCF_2H/SF_5OCHFCF_2Cl$, 8/92) than that found for the bromine-containing compound ($SF_5OCFBrCF_2H/SF_5OCHFCF_2Br$, 20/80).

The second attempted approach to the synthesis of $SF_5OCF=CF_2$ was by the following six step synthesis:

1. $$\begin{matrix} CF_2{-}C{=}O \\ | \quad\quad O \\ CF_2{-}C{=}O \end{matrix} + ROH \longrightarrow \begin{matrix} CF_2{-}COOR \\ | \\ CF_2{-}COOH \end{matrix}$$

2. $$\begin{matrix} CF_2{-}COOR \\ | \\ CF_2{-}COOH \end{matrix} + NaOH \longrightarrow \begin{matrix} CF_2COOR \\ | \\ CF_2COONa \end{matrix}$$

3. $$\begin{matrix} CF_2{-}COOR \\ | \\ CF_2{-}COONa \end{matrix} \xrightarrow[\Delta]{} CF_2{=}CFCOOR + NaF + CO_2$$

4. $$CF_2{=}CFCOOR + SF_5OF \longrightarrow SF_5OCF_2CF_2COOR$$

5. $$SF_5OCF_2CF_2COOR \xrightarrow[b.\ \ \Delta]{a.\ NaOH} SF_5OCF{=}CF_2$$

This route has the added attraction that other monomers may be similarly prepared. Thus with perfluoroglutaric anhydride $SF_5OCF_2CF{=}CF_2$ or $CF_3OCF_2CF{=}CF_2$ may be prepared. Most of these steps are simple and straightforward with the exception of step 3, decarboxylation of the salt-ester. The only reference to a reaction which may have some bearing on the present synthesis is the pyrolysis of disodium perfluoroadipate[21] which

(21) Barney, A. L., U. S. Pat. 2,437,148(1948).

gave a 30% yield of the butadiene.

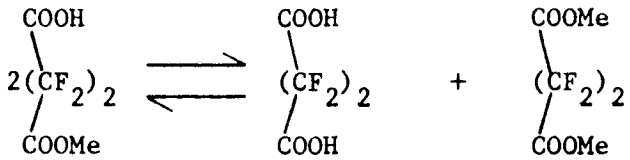
6. Preparation of CF_2=CFCOF

In our initial attempt to pyrolyze crude $CF_3CH_2OOCCF_2CF_2COONa$, one of the major products was a compound which exhibited infrared absorption maxima at 5.39 and 5.73μ. The position of the maximum at 5.39μ did not appear at the time to be consistent with that of either the trifluorovinyl group or the ester carbonyl group. Neither maximum, attributable to these groups, would be expected below 5.6μ particularly in view of the usual shift to longer wave lengths due to conjugation. The subsequent identification of this compound, by NMR analysis, as perfluoroacrylyl fluoride makes the assignment of the 5.39μ maximum consistent with absorption due to an acid fluoride carbonyl. The maximum at 5.73μ may also be assigned to absorption due to the trifluorovinyl group with a small shift due to conjugation with the carbonyl oxygen.

The presence of perfluoroacrylyl fluoride and the total absence of the acrylic ester in the initial pyrolysis was quite unexpected.

It was found in later experiments, however, that in the preparation of the salt-ester, ester hydrolysis was occurring, resulting in a precipitate of mainly the disodium salt. Thus, the starting material for the initial pyrolysis reaction, although known to have contained some ester-salt, probably contained a high proportion of the disodium salt. This would appear to be true since subsequent reactions have shown that pyrolysis of the disodium salt results in about a 40% crude yield of CF_2=CFCOF. (A subsequent larger scale reaction indicated a considerably lower yield.) In view of this unusual decarboxylation it appeared likely that the salt-ester should also decarboxylate to give the acrylic ester.

In attempts to prepare the salt-ester it was found that on neutralization of the ester-acid with NaOH, hydrolysis of the ester group occurs rapidly at a pH above 7. In addition, it was also found that the ester-acid equilibrates, on standing, resulting in precipitation of the dicarboxylic acid.



Pyrolysis of the salt-ester prepared by carefully neutralizing the salt-acid yielded CF_2=CFCOF with no indication of the presence of CF=CFCOOMe. (Although the purity of this salt-ester was assumed to be high, the results of the pyrolysis would indicate the probable presence

of some disodium salt.)

In considering Ref. 21, it would appear likely that decarboxylation of disodium perfluorosuccinate would yield FC≡CF(which explodes when condensed) rather than CF_2=CFCOF. In our first pyrolyses precautions were taken in the event that some disodium salt was present. Little evidence has thus far been found which would indicate the presence of FC≡CF other than two unidentified trace GLC peaks with retention times less than that of CF_2=CFCOF.

A fairly straightforward two-step mechanism may be proposed whereby decarboxylation occurs initially to yield sodium acrylate.

$$NaOOCCF_2CF_2COONa \xrightarrow{\sim 300^\circ} CF_2{=}CFCOONa + NaF + CO_2$$

Since the salt is nonvolatile and is formed as an intimate mixture with NaF, a second reaction may occur in which the acid fluoride is formed <u>in situ.</u>

$$CF_2{=}CFCOONa + NaF \xrightarrow{\sim 300^\circ} CF_2{=}CFCOF + Na_2O$$

In order to determine whether the second step in this reaction does in fact occur, a mixture of C_2F_5COONa/NaF was heated to decomposition under vacuum. No propionyl fluoride was detected. Although it would appear from this that replacement of ONa by F is occurring in a different manner it is conceivable that a displacement of this nature is unique with the perfluoroacrylates.

An initial small scale attempt was carried out corresponding to Steps 4 and 5a under Section 5.

1. $CF_2{=}CFCOF + SF_5OF \longrightarrow SF_5OCF_2CF_2COF$

2. $SF_5OCF_2CF_2COF + H_2O \longrightarrow SF_5OCF_2CF_2COOH$

On reaction of SF_5OF with acrylyl fluoride, in Step 1, the infrared maxima at 5.73 and 5.39μ disappeared and a new maximum appeared at 5.30μ. This new maximum is consistent with the carbonyl of a saturated acid fluoride. In addition, a strong, broad maximum at 11μ is attributable to SF_5 absorption. Hydrolysis and neutralization shifted the carbonyl absorption from 5.30 (COF) to 5.63 (COOH) to 5.95μ(COONa).

Unfortunately, only a trace amount of the sodium salt was made. No attempt has yet been made to pyrolyze this salt.

It is interesting to speculate concerning the homopolymerization of CF_2=CFCOF. In the light of a report[22] on radical reactions of the carbonyl function of $(CF_3)_2C$=O, it is conceivable that perfluoroacrylyl fluoride will polymerize, at least to a limited extent, through 1,4 addition. This would present a method for introducing a heteroatom in the polymer chain, to give $-(-CF_2-CF=CF-O-)-_x$

7. Attempted Synthesis of CF_2=CFC(OCF_3)=CF_2

In our continuing effort to determine the effect of structure on low temperature properties of polymers, the elastomeric properties of copolymers of CF_2=CFCH=CH_2 with chlorine-containing vinyl monomers suggested the possible good low termperature properties of the titled monomer.

The following reaction sequence was devised for this synthesis.

1. $CF_3OF + \overline{CF_2CF_2CCl=CCl} \longrightarrow \overline{CF_2CF_2CFClCClOCF_3}$

2. $\overline{CF_2CF_2CFClCClOCF_3} \xrightarrow[EtOH]{Zn} \overline{CF_2CF_2CF=COCF_3}$

3. $\overline{CF_2CF_2CF=COCF_3} \xrightarrow{500\text{-}600^\circ} CF_2$=CFC($OCF_3$)=$CF_2$

Steps 1 and 2 were carried out without difficulty and the desired olefin was obtained in good yield. However, pyrolysis of the methoxy-substituted cyclic olefin did not yield the butadiene. Although this ring opening reaction is reported[23] to give good yields of the corresponding butadiene, in the pyrolysis of $\overline{CF_2CF_2CF=C(OCF_3)}$ carbonization occurred and COF_2 was noted in the pyrolyzate.

It would appear from this that the presence of an OCF_3 group reduces the thermal stability of the cyclobutene and/or the butadiene. This appears to be substantiated by the observation that polymers containing high proportions of $CF_3OCF=CF_2$ appear to decompose at temperatures as low as 150°.

(22) Unpublished work of C. G. Krespan given at a seminar at the University of Florida, 1965.

(23) J. L. Anderson, R. E. Putnam, and W. H. Sharkey, J. Am, Chem. Soc., 83, 382(1961).

In addition to the decomposition products, a small amount of unidentified product was obtained which exhibited a strong infrared maximum at 5.80μ and a weak maximum at 5.5μ.

8. Attempted Preparation of $(CF_3)_2CFOCF=CF_2$

In a recent paper by Pittman and Sharp[24] it was shown that potassium perfluoroisopropoxide may be prepared by reaction of hexafluoroacetone with KF. This preparation once again suggested the use of this alkoxide for the preparation of a new vinyl ether. Thus by analogy to the addition of the hydrocarbon alkoxides it was considered probable the following reactions might occur.

$$(CF_3)_2C{=}O + KF \longrightarrow (CF_3)_2CFOK \xrightarrow{C_2F_4} (CF_3)_2CFOCF{=}CF_2 + KF$$

Unfortunately, as in other attempts at similar reactions,[25] KF reacted with the acetone to form the alkoxide but subsequent reactions with C_2F_4 did not yield the desired vinyl ether. Graham[26] has shown that perfluoro(α-olefins) will react, in the presence of a metal fluoride and a polar solvent, with carbonyl compounds to give the corresponding perfluoro tertiary alcohols.

$$(CF_3)_2C{=}O + CsF + C_2F_4 \longrightarrow (CF_3)_2C(OCs)(C_2F_5) \xrightarrow{H^+} CF_3C(CF_3)(OH)(C_2F_5)$$

(24) A. G. Pittman and D. L. Sharp, Poly.Let., B3, 379(1965).

(25) Second Annual Report, this contract.

(26) D. P. Graham and V. Weimays, Paper 15a, Division of Fluorine Chemistry, Abstracts 150th Meeting of ACS, Sept. 1965.

From the conditions used in our attempt at this reaction it would appear that the alkoxide was formed but not liberated as the free alcohol by acidification. This would account for the apparent loss of C_2F_4.

9. Reaction of C_2F_5COOH with FSO_3H

Although the method presently used for preparation of acid fluorides (reaction of an acid chloride with ZnF_2) gives excellent yields, reaction time is generally quite long. In an attempt to speed up this preparation the recommendations of an Allied Chemical Company technical bulletin[27] were tried. Reaction of C_2F_5COOH with FSO_3H, at reflux, gave the desired acid fluoride but only in low yield.

(27) Allied Chemical Co., Tech. Bul. TA-20711, Fluosulfonic Acid.

EXPERIMENTAL

The CF_3OF used in some of these syntheses was prepared by reaction of elemental fluorine with CO as described by Porter and Cady.[28] The purity of the CF_3OF was estimated to be 70% with the major impurities being COF_2, CF_4 and $(CF_3O)_2$. In reactions of CF_3OF with olefins the crude reaction product was used after F_2 was removed.

Chromatographic analyses were run at room temperature on a non-commercial gas chromatograph. The detection system was a thermal conductivity cell and helium was used as the carrier gas. The columns were 3/8" I. D. Pyrex glass, 8' long, packed with HMDS/Chromosorb with 25% ethyl ester of Kel-F acid 8114 as the stationary phase. Exceptions are noted in the text.

Infrared analyses were obtained using a Beckman IR-5.

NMR spectral analyses were carried out at RT using a Varian high-resolution nuclear magnetic resonance spectrometer model V-4300-2, provided with field homogeneity control, magnetic insulation and super-stabilizer. Chemical shifts were determined by side-bands applied with an audio oscillator for which the frequency is continuously monitored by an electronic counter. Unless otherwise noted, the chemical shifts for fluorine are given with respect to external CF_3COOH and the chemical shifts for hydrogen are given with respect to external CH_3CHO.

A. Polymers

1. High Pressure Polymerization

We are presently able to carry out small scale polymerization reactions at pressures up to 1300 atm. The pressure is generated by using hydraulic pressure to collapse a thin-wall metal tube containing the monomer or monomers.

Typically, the monomer is added to an evacuated nickel tube (99.5% Ni, 6" x 3/8" O.D., 0.035" wall) which is sealed at one end by crimping and sealing with soft solder. While maintaining the lower part of the tube at -196° the tube is crimped adjacent to the vacuum tubing connection and with the crimping tool in place, to hold a vacuum seal, the tube is removed from the vacuum system and the upper crimp sealed with soft solder.

(28) Roger S. Porter and George H. Cady, U. S. Pat, 3,100,803.

The polymerization tube is placed in a water filled, high pressure reactor (73 cc capacity), the reactor sealed and the system pressurized with a hand operated hydraulic pump.[29] When using Co^{60} initiation the apparatus is disconnected from the pump (a ball check valve prevents loss of pressure) and placed in a vertical position centered about 5 cm from the Co^{60} source. The radiation flux is approximately 7×10^5 r/hr.

At termination of polymerization the polymerization tube is removed from the reactor, cooled with liquid N and a saw cut made in the tubing to remove unpolymerized monomer. While still at -196° the polymerization tube is placed in a tube attached to the vacuum system, the system evacuated and the amount of residual monomer determined by volume.

a. Co^{60} Initiated Homopolymerization of C_2F_4 (TFE) and $CH_2=CF_2$ (VF_2)

In an initial attempt to try the high pressure polymerization technique described above, 24.4 mM of TFE and 24.4 mM of VF_2 were homopolymerized simultaneously at a starting pressure of 1200 atm. The reactor was exposed to gamma rays for a total of 47.5 hours at ambient temperature. At the end of the irradiation period the pressure in the reactor had dropped to 904 atm. On opening the polymerization tubes only a trace of TFE monomer was recovered indicating essentially total conversion to polymer. The resultant polymer was a white, brittle, wax-like solid which molded into a tough homogeneous film at about 350°. The VF_2 polymerization gave 77% (1.62%/hr.) conversion to a hard, opaque polymer which molded into a hard transparent film.

b. Copolymerization of CF_3NO with MVE, EVE, PVE and PVM

Using the same high pressure system described above, several "nitroso" polymers containing pendent trifluoromethoxy groups were prepared (Table II). This is a self-initiating system, requiring no initiator, which invariably yields an alternating polymer.

In the initial polymerization attempt (Exp. 1P), while pressurizing the system, reaction occurred at a pressure of about 810 to 950 atm, which caused a surge in pressure to 1,200 atm. Only a trace of polymer was obtained in this reaction. Subsequent reactions, which were carried out below this apparent "critical" pressure, yielded elastomeric polymers.

(29) Enerpac Model 82-102, Enerpac Test Systems, Butler, Wisc.

TABLE II

HIGH PRESSURE POLYMERIZATION[a]

Exp. No.	Monomer (mM)[b]	Pressure Atm.	Time Hrs. at P(T)	Recovered Monomer (mM)	% Conv.	Polymer Character
1P	MVE(13.7), CF_3NO(17.5)	Reaction occurred at 810 to 950 atm. causing a surge to 1200 atm., tube seal opened.				
2P	MVE(9.0), CF_3NO(10.4)	610-680	11(RT)	2.45	87,5	1 g, Elastomer.
3P	MVE(17.4), CF_3NO(19,1)	470-680	17(0°)	6,5	82	Elastomer tougher than 2P.
4P	MVE(17.8), CF_3NO(17.7)	430-680	11(0°)	13.9	61	Elastomer.
13P	MVE(11.1)/C_2F_4(10.0)	1000-1200 (50-60°)	61,5	8,5	59,6	Molded at 320° to a clear, tough film.
15P	MVE(11.2)/TB(11.8)	1000-1300	22 (50-60°)	10.0	86.9	Elastic porous polymer, very difficult to mold but thin sections tough elastomer. 3-8% MVE.
19P	MVE/C_2F_4/C_2H_4 (7.7)/(18.0)/(5.4)	About 1,400 to >2,700	- (80°)	Decomposed, IR of recovered gases indicate CF_4, COF_2		
20P	MVE(11.7)/VF_2(17.5)	"	(80°)	10,5	64	50.8 mole % MVE, melt range ∿245°, molds to tough elastomeric film.
22P	MVE(29.1)/VF_2(43.5)	925-1230	22.5(70°)	(3,1 g, polymer)	-	Elastomeric sponge
23P	MVE(25.2)/VF_2(38.5)	1000	∿16(85-90°)	29.0	54.5	Weak gum.
24P	MVE(30.4)/VF_2(48.2)	1000	∿16(85-90°)	37.9	52.3	Weak gum.
29P	MVE(26.0)/VF_2(74.9	1000 to 1200	19(100°)	56.4	44.1	Molded at 150° to elastomeric film.

TABLE II
(continued)

HIGH PRESSURE POLYMERIZATION[a]

Exp. No.	Monomer (mM)[b]	Pressure Atm.	Time Hrs. at P(T)	Recovered Monomer (mM)	% Conv.	Polymer Character
30P	MVE(26.2)/VF_2(75.0)	1000 to 1200	19(100°)	38.6	61.8	Molded at 110-120° to elastomeric film.
31P	MVE(25.5)/VF_2(51.9)	760 to 1000	26(100°)	-	42.7	Same as above.
42P	MVE(7.2)/VF_2(28.6)	1000	44.5(105°)	10.5	71.1	Tough elastomer.
27P	MVE(12.3)/TFE(12.3)/C_2H_4(12.2) -- Decomposed.					
5P	PVM(10.1)CF_3NO(9.44)	430-680	11(0°)	16.3	16.4	0.45 g. brittle plastic.
10P	PVM(5.0)/CF_3NO(5.2)	1000	136(RT)	Mostly oxazetidine	-	Brittle, clear plastic melts to a tacky liquid.
12P	PVM(10.1)/C_2F_4(11.2)	1000-1200	61.5 (50-60°)	9.3	56.4	Melts at 314°, molded to a clear, tough, flexible film. 85 mole % TFE.
14P	PVM(22.5)/C_2F_4(22.1)	1000-1300	22(50-60°)	29.1	33.8	Molded at 320°. Transparent film.
16P	PVM(15.2)/C_2F_4(16.9)	1160	64(50-60°)	20.1	37.4	Some decomposition. Carbon in polymer.
33P	PVM(6.8)/VF_2(23.0)	1000 to 1180	23(105°)	19.2	35.6	Molded at 160° to a clear, tough film. m.p. 150-160°.
35P	EVE(22.7)/VF_2(72.3)	1700+	Decomposed, recovered 5.37 g. black residue, mostly carbon.			
36P	EVE(7.2)/VF_2(24.0)	750 to 1150	13.5(93°)	7.7	75	Molded at 110-120° to an excellent tough elastomer, 18 mole % EVE.

TABLE II
(continued)

HIGH PRESSURE POLYMERIZATION[a]

Exp. No.	Monomer (mM)[b]	Pressure Atm.	Time Hrs. at P(T)	Recovered Monomer (mM)	% Conv.	Polymer Character
39P	EVE(15)/CF_3NO(15.6)	685	16.3(0°)		31	1.5 g. tough elastomer T_g = -25 to -7.5°.
40P	EVE(16.7)/VF_2(49.4)	1000 to 1230	16.5 (103°)	47.6	28	
34P	MVEH(5.3)/VF_2(16.1)	1000 to 1180	23(105°)	10.8	49.2	Molded at 190° to an elastomeric film.
44P	PVE(36.4)/CF_3NO(37.3)	685	16(0°)		33	Tough gum.
45P	PVE(16.6)/VF_2(49.4)	1000	13.5(87°)			Upper portion molded at 150°, tough elastomer, 10 mole % PVE. Lower portion molded at 185°, clear plastic, 4 mole % PVE.

(a) Reactions run in 7.5 mm I.D. Ni tubes except 22P, 10 mm I.D. Ni tube, initiator, 0.1 to 0.3 wt. % asobisisobutyronitrile.

(b) MVE, $CF_3OCF=CF_2$; PVM, $(CF_3O)_2C=CF_2$; EVE, $C_2F_5OCF=CF_2$; PVE, $C_3F_7OCF=CF_2$; VF_2, $CH_2=CF_2$; TFE, $CF_2=CF_2$; MVEH, $CF_3OCH=CF_2$; TB, $CF_2=CFCH=CH_2$.

The glass transition temperature of MVE, EVE and PVE copolymers, obtained using the viscous flow apparatus, are shown in Table III. Infrared spectra of "nitroso" copolymers containing pendent OCF_3, OC_2F_5 and OC_3F_2 groups are shown in Figures 1, 2 and 3.

TABLE III

Glass Transition Temperature of Some Perfluoro(vinyl ether) Copolymers[a]

No.	Monomers*	Polymer Compn. Wt. %	T_g
22P	MVE/VF_2	53/47	-31°, -35°, -35.5°
24P	MVE/VF_2	49/51	-32°
26P	MVE/VF_2	51/49	-42°, -38°
36P	EVE/VF_2	43/57	-30°, -28°, -25°
45P-1	PVE/VF_2	31/69	31.5°, 31.5°, 30.5°
185	PVM/VF_2	31/69	-51°
159	MVEH/VF_2	57/43	-25°

*VF_2, $CF_2=CH_2$; MVE, $CF_3OCF=CF_2$; EVE, $C_2F_5OCF=CF_2$; PVE, $C_3F_7OCF=CF_2$, MVEH, $CF_3OCH=CF_2$; PVM, $(CF_3O)_2C=CF_2$

(a) T_g's determined on a recently constructed viscous flow apparatus similar to that described by S. A. Arzhakov, et al., Doklady Physical Chem. Proc. of the Akad. Sci., 154(1), 5(1964).

The use of this apparatus for determining T_g has not been completely evaluated. Duplication appears to be fair, as shown for several of the samples, and close agreement with DTA values for a MVE/CF_3NO copolymer was observed (Table I). However, the values determined for MVE/VF_2 copolymers do not agree well with DTA values previously obtained (Second Annual Report). In view of this uncertainty, the values given in this table are only considered as approximate.

Copolymerization of CF_3NO/PVM was initially attempted using PVM which had been purified by distillation through a 300 mm packed distillation column. The PVM contained 22.2% of a mixture of isomers identified by NMR analysis as $CF_3OCF{=}CFCl$ and $CF_3OCCL{=}CF_2$ plus 2.3% of unidentified impurities. Only a small amount of brittle polymer was obtained in this reaction (5P Table II). As with other copolymers of the fluorocarbon vinyl ethers and CF_3NO appreciable amounts of cyclic "dimer" $CF_3NCF_2C(OCF_3)_2O$ were also obtained. Infrared spectra for the oxazetidines obtained as by-products in these copolymerization attempts are shown in Figures 4, 5 and 6.

NMR Data for $CF_3\overline{NCF_2CF(OCF_3)O}$

Designation	Chemical Shift ppm	Pattern and Splitting cps	Rel. Area	Assignment
Fa	+55.4($CFCl_3$)	1°	2.0	OCF_3
Fb	+70.0($CFCl_3$)	3° x 7.6	1.0	NCF_3
Fc	+95.3($CFCl_3$)	Broad	0.87	CF_2

c. Copolymers of $CF_3OCF{=}CF_2$(MVE) $C_2F_5OCF{=}CF_2$(EVE), $C_3F_7OCF{=}CF_2$(PVE) and $(CF_3O)_2C{=}CF_2$(PVM)

Using the high pressure polymerization techniques described above, a variety of fluorocarbon vinyl ether copolymers were prepared using 0.1 to 0.3 wt. % azobisisobutyronitrile as the initiator (Table II). Polymerizations were generally carried out at 1000 atm. pressure and between 50° and 105°.

In the high pressure polymerization of TFE/PVM (16P) some carbonization occurred indicating decomposition of the TFE. In 19P, using a molar ratio of TFE/MVE/C_2H_4(1/0.43/0.3), decomposition also occurred, but to a much greater extent, causing a surge in pressure from 1,400 to greater than 2,700 atm. This pressure surge exceeded the limit of a 29,000 psi gage and ruptured a brass gasket in the reactor.

The reaction apparently was quenched rapidly enough to prevent rupture of the nickel polymerization tube. An infrared spectrum of the recovered gases showed characteristic maxima of CF_4 and COF_2 and the reaction tube contained carbon. A second polymer sample, 20P, run concurrently with 19P, in which a molar ratio of 1.5 VF_2/MVE was reacted, polymerized to an excellent tough elastomer.

Approximately equimolar quantities of PVM/C_2F_4 were copolymerized (12P and 14P, Table II), to give a copolymer containing 15 mole % PVM. This polymer flowed readily at 320° under pressure to give a clear, tough film. An infrared spectrum of this copolymer is shown in Figure 7. In 16P, where a slight excess of C_2F_4 was used, some carbonization occurred. No pressure surge was noted in this instance.

2. Radiation Induced Polymerization

In the polymerization attempts summarized in Tables IV and V, the monomer proportions were measured volumetrically on a calibrated vacuum system, condensed into a 13 ml. capacity Carius tube and sealed under vacuum. The reaction tubes while still frozen were placed in a sample holder containing six copper tubes concentrically spaced 1.91 cm. from the center of a central 1.78 cm. I.D. tube. The samples and sample holder were warmed to room temperature or the indicated temperature, then placed in the radiation chamber and the Co^{60} capsule lowered into the central tube. The radiation flux was approximately 7 x 10^5 r/hr. and the total gamma dose for each sample is shown in the Tables. Irradiation of these samples was carried out at the University of Florida, Gainesville, Florida, through the assistance of Dr. R. J. Hanrahan of the Department of Chemistry.

Copolymers of TFE/MVE, 223 (containing 34.7 wt. % MVE) and 235 through 239 (containing 44.6 wt. % MVE) were molded into film and submitted to the Materials Division for further evaluation. Sample 223 molded easily at 290 to 315° at 4000 psi to give a clear, tough film. Attempts to mold the combined copolymers 235 to 239 at the same temperature gave a film containing numerous bubbles. By trial and error 235-9 was found to mold easily at 145° and 3000 psi. Qualitatively, the character of these two copolymers differ considerably. An increase in the vinyl ether content appears to increase the flexibility but also appears to result in a decrease in strength.

TABLE IV

Gamma Ray Initiated Polymerization[a]

Exp. No.	Monomer (mM)[b]	Gamma Dose Rep. x 10^6	% Conv.	Conv. Rate %/hr.	Polymer Compn. Mole %	Polymer Character
222	MVE/(3.6)/TFE(12.9)	4.39	98.2	>6	22/78	Molded at 320° to a flexible film.
223	MVE(4.5)/TFE(12.1)	4.39	89.5	5.8	24/76	"
223A,B	MVE(16.9)/TFE(50.4)	4.76	90,8	5.8	24/76	"
224	MVE(5.6)/TFE(12.4)	4.4	76.8	5.0	-	"
225	MVE(8.4)/TFE(8.4)	4.4	27.6	1.8	68/32	More elastic than previous polymers containing less ether. m.p. 265.
231	MVE/TFE/C_2H_4 (3.8)/13.4)/1.8)	4.7	95.5	>5.9	17/73/10 m.p. 370	
232	(3.6)/10.7)/2.5)	4.7	98.5	>5.9	21/64/15 m.p. 358	White spongy polymer, appears inhomogeneous when molded.
233	(3.4)/(9.7)/(3.4)	4.7	97.5	>5.9	20/59/21 m.p. 265	
226	MVE(3.4)/TBD(13.4)	4.8	78.8	1.65	TBD 100%	White elastic solid, could not be molded.
227	MVE(4.2)/TBD(12.6)	4.8	74.5	1.56	TBD 100%	"
228	MVE(5.6)/TBD(11.2)	4.8	65.0	1.37	TBD 100%	"
229	MVE(8.4)/TBD(8.4)	4.8	48.8	1.02	TBD 100%	"

TABLE IV
(continued)

Gamma Ray Initiated Polymerization[a]

Exp. No.	Monomer (mM)[b]	Gamma Dose Rep. x 10^6	% Conv.	Conv. Rate %/hr.	Polymer Compn. Mole %	Polymer Character
235-40	MVE(50.4)/TFE(50.4)	1.3	60.1	1.28	32.7/67.3	Molded at 145° to a flexible film.
248-50	MVE/TFE/C_2H_4 (6.7)/(20.2)/(6.7)	4.9	100.0	>5.73	1/3/1	Molded at 320° to mottled film.
252	MVE(1.4)/TFE(8.4)	5.1	100.0	>5.48	14.2/85.8	Molded at 320° to clear tough film.
253	MVE(1.4)/TFE(7.0)	5.1	100.0	>5.48	16.6/83.4	
254	MVE(1.4)/TFE(9.8)	5.1	100.0	>5.48	12.5/87.5	
217	MVE(3.06)/HFB(11.9)	13.6	39.9	.8		Infusible white powder.
218	MVE(8.0)/HFA(7.6)	13.6	8.9	.19		Traces of tacky oil.
203,4, 5,6	PVM(13.9)/VF_2(42.8)	12	75	1.7[d]	13/87	Flexible, spongy, white solid. Highly swollen in acetone.
209,10 11	PVM(11)/VF_2(33)	5	42	2.3[e]	13/87	Same as above except forms a gel in acetone.
203A	PVM(4.14)/VF_2(117.)[c]	13.3	43	1.0		High viscosity liquid or tacky gum.
230	PVM(3.2)/TFE(12.6)	4.7	78.5	4.6	5/95	Molds at 230° to a brittle solid.
234	PVM(4.2)/TFE(8.4)	4.7	11.1	0.27	41/59	Viscous, tacky liquid.

TABLE IV
(continued)

Gamma Ray Initiated Polymerization[a]

Exp. No.	Monomer (mM)[b]	Gamma Dose Rep. x 10^6	% Conv.	Conv. Rate %/hr.	Polymer Compn. Mole %	Polymer Character
242-47	MVE(37.2)/TFE(74.5)	26.3	93.0	0.99	30/70	
278	EVE(5.5)/TFE(16.2)	3.6	100	>6.7	25/75	Molded at 330° to a mottled, hazy film.
279	EVE(5.75)/TFE(23)	3.6	100	>7.7	20/80	"
280	EVE(6.9)/CF_3NO(6.9)	No initiator at room temperature for 1 week.				0.55 g. of tacky elastomer, mostly oxazetidine.
200	$CF_3OCH=CFCl$(3.75) VF_2(11.25)	50.5	15.3	0.08		Viscous oil.
201	$CF_3OCH=CFCl$(7.66) VF_2(7.66)	58	30.8	0.01		Oil
213 14,15	HFB(44.9)	11.3	95	2.3[d]		Insusible white powder
216	HFB(6.96)/PB(6.96)	11.3	9.4			Trace of tacky liquid.
219	HFA(7.16)/TFE(7.4)	13.6	52	1.07		White, friable, waxy powder. m.p. 320°.

(a) Radiation flux 7 x 10^5 r/hr.

(b) MVE, $CF_3OCF=CF_2$; PVM, $(CF_3O)_2C=CF_2$; VF_2, CF_2CH_2; HFA, CF_3COCF_3; TBD, $CF_2=CFCH=CH_2$; TFE, C_2F_4; PB, $CF_2=CFCF=CF_2$; HFB, $CF_3C\equiv CCF_3$.

(c) In addition, contained 0.64 mM $CF_3OCF=CFCl$, $CF_3OCl=CF_2$ mixt. and 0.35 mM $CF_3OCH=CFCl$.

(d) Average of four runs.

(e) Average of three runs.

TABLE V

CF_3CHO Polymers[a]

Exp. No.	Monomer (mM)[b]	Gamma Dose Rep. x 10^6	% Conversion	Conversion Rate %/hr.	Polymer Description
221	TAA(2.4)/C_2F_4(2.4)	1.8	14	0.22	Brittle solid.
251	TAA(13.3)	(3 mole %$BF_3 \cdot Et_2O$)	82	-	Viscous liquid.
255	TAA(8.2)/C_2F_4(8.4)	5.1	61	3.25	Molded at 310° into a flexible, clear film.
257	TAA(2.8)/C_2F_4(5.6)	6.3	100	>4.4	Appears to be a mixture of both homopolymers plus aldehyde trimer.
258	TAA(5.6)/C_2F_4(2.8)	6.3	98	>4.4	Upper portion of tube white powder, lower portion pasty solid. Appears to be mixture of polymers
259	TAA(4.2)/C_2F_4(4.2)	6.3	97	>4.4	
256	TAA(16.8)	No irradiation, trimerized spontaneously on warming.			
261	TAA(8.4)/PP(8.4)	63	53	2.33	Pasty material having strong aldehyde odor. Volatilizes on heating at high temperature.
262	TAA(7.3)/PB(7.3)	63	52	2.28	"
266	TAA(16.1)/C_2F_4)(16.1)	7.9	60	2.1	Molded at 320° into an opaque, brittle, waxy film.
268	TAA(2.9)	13.4	100	-	Colorless oil.

TABLE V
(continued)

CF_3CHO Polymers[a]

Exp. No.	Monomer (mM)[b]	Gamma Dose Rep. x 10^6	% Conversion	Conversion Rate %/hr.	Polymer Description
270	TAA(0.6)/TFE(5.2)	12.6(-78°)	100	-	Molded at 330° to a transparent film containing cracks. 10/90 mole % comp.
271	TAA(1.2)/TFE(4.6)	12.6)-78°)	100	-	Same as above. 20/80 mole % comp.
272	TAA(2.3)/TFE(3.5)	12.6(-78°)	100	-	Would not fuse at 330°. 40/60 mole % comp.
275	TAA(15.6)	6.7(-78°)	77	.33	Tacky polymer.
276	TAA(7.50)/PO(8.06)	12.6	51	1.05	Looks like homopolymer.
281-3	TAA(65.2)/TFE(11.4)	12.8(-78°)	96-99%	-	Molded at 320°, 6000 psi brittle waxy polymer.
277	TAA(38.0)	Initiated with 2μ 1. $BF_3 \cdot Et_2O$ - RT(100 hrs.)			Tacky polymer.
RH39-A	TAA(51)	Initiated with 5.7mM $BF_3 \cdot Et_2O$ - 0° - RT(24 hrs.)			Viscous liquid.
RH39-B	TAA(51)	Initiated with 2.7mM $BF_3 \cdot Et_2O$ - 0° - RT(24 hrs.)			Viscosity >39A.
RH39-C	TAA(50)	Initiated with 1.0mM $BF_3 \cdot Et_2O$ - 0° - RT(24 hrs.)			5.3 g. Viscosity >39B, IR indicates OH.
RH41-B	TAA(200)	Initiated with 4.0mM $BF_3 \cdot Et_2O$ - 0° - RT(24 hrs.)			Polymer decomposed in H_2O.

(a) Radiation flux 7 x 10^5 r/hr.

(b) TAA, CF_3CHO; PP, $CF_3CF{=}CF_2$; PB, $CF_2{=}CFCF{=}CF_2$; TFE, C_2F_4; PO, $CF_3\overline{CFCF_2O}$.

Infrared spectra of typical VF_2/MVE, VF_2/EVE, and VF_2/PVE copolymers are shown in Figures 8, 9 and 10.

Terpolymer Samples (combined 248-50 C_2F_4/C_2H_4/MVE, 1/0.3/9.3) would not mold into a homogeneous film. When molded at 330° and 6000 psi the polymer flowed readily but gave a film having a mottled appearance and numerous cracks. Portions of the film which were clear appeared to have improved extensibility over that of a 4/1 C_2F_4/MVE copolymer.

In several instances attempts to homopolymerize CF_3CHO(TAA) using gamma ray initiation, resulted in spontaneous polymerization, before irradiation, to the trimeric "para" aldehyde. This product volatilized between 110 and 160°. Copolymerization of TAA with an equimolar amount of C_2F_4, (Table V, 255), using gamma ray initiation yielded a white polymer which molded into a tough clear film at 310° and contact pressure. An infrared spectrum of this copolymer is shown in Figure 11. A comparative infrared spectrum of a low molecular weight homopolymer of TAA is shown in Figure 12.

Other attempts to prepare copolymers were not successful.

3. Emulsion Polymerization of $CF_2=CFCH=CH_2$

Into a 40 ml. heavy wall Pyrex ampule was placed 9 ml. of solution "A".

Solution A

H_2O	900 g.
Tide	25 g.
5% aq. $C_7F_5COONH_4$	5 g.
Dodecyl Mercaptan (pH adj. to 10)	1.5 g.

Solution B

1.5% solution $(NH_4)_2S_2O_8$

The ampule was frozen in liq. N_2, evacuated and 1 ml. of solution "B" added, followed by 14 mM (1.6 g.) of $CF_2=CFCH=CH_2$. The ampule was sealed and tumbled end over end in a water bath at 45 to 50° for two hours. At the end of this time the ampule was frozen and opened to the vacuum system, no monomer was recovered. The suspended polymer was precipitated with HCl, washed with water and dried at 100° under vacuum yielding 1.4 g. of a slightly off-white crumb. A small amount of the polymer was molded into a thin, tough leathery, film. DTA analysis of this polymer is shown in Table VI.

4. CF_3OF Initiated Polymerization

a. C_2F_4

Into an evacuated 100 ml. capacity Pyrex glass ampule was condensed about 0.05 mM of CF_3OF. The upper portion of the ampule was then cooled to -196° and 1.1 mM of C_2F_4 added. The ampule was sealed and allowed to warm to room temperature. Immediately upon warming a trace of white solid was noted on the walls of the ampule. After several days at room temperature no additional polymers appeared to form. No attempt was made to determine the extent of conversion to polymer.

b. $CF_2=CFCl$

Into a 27 ml. capacity Pyrex glass ampule was condensed 5 ml. of Freon 113($CF_2ClCFCl_2$). The ampule was cooled to -196°, evacuated, and 3.9 mM of CF_2CFCl added. The frozen mixture was melted, mixed, then refrozen and 0.59 mM of CF_3OF added. The ampule was sealed and allowed to warm to R.T. After several days the ampule was reopened to the vacuum system and the volatiles removed leaving a trace of high boiling liquid.

5. Poly(ethylene perfluoroglutarate)

A mixture containing 175.4 g. (0.76 mole) of perfluoroglutaric acid and 105 g. (1.7 moles) of ethylene glycol was charged into a three-neck flask equipped with stirrer, nitrogen inlet tube, and 10 inch Vigreaux distilling column and head. The mixture was slowly heated to 200° to distill off water. When water stopped distilling the pressure was gradually reduced to about 0.5 mm and glycol was distilled off at 200° for five hours. The resulting polymer was viscous syrupy material which had a molecular weight of 4,500 as determined by vapor pressure osmometry in tetrahydrofuran solvent.

TABLE VI

DTA Polymer Analysis[a]

Exp. No.	Polymer Composition (mole %)	Probable T_g	Other Transitions[b]
1001-12-1	$CF_2=CFCH=CH_2$ (100)	-37°	-37° En., 38° En., 93°, start dec. 282°, 370° and 404° Ex.
3P	CF_3NO(50) $CF_3OCF=CF_2$(50)	-5°	-5° En., 37° En., Ex. start at 100 peak at 305°.
152	$CF_2=CH_2$(63.6) $CF_3OCF=CF_2$(50)	-52°	-52° En., -42° En., -14° En., 55° En., 108° En. Start Ex. 350° peak at n 485°.

(a) By Sadtler Research Laboratories, Inc., Phila., Pa. DuPont 900 differential thermal analyzer 20°/min., N_2 atm.

(b) En., endotherm; Ex., exotherm.

6. Attempted Chain Extension and Curing of Poly(ethylene perfluoroglutarate)

A 23.0 (0.005 equiv.) g. sample of the polyester was charged into a 50 ml. micro resin kettle and stirred at 120-30° under nitrogen while 2.6 (0.015 equiv.) g. of toluene-2,4-diisocyanate was added all at once. The mixture was stirred for 45 minutes and then degassed for 45 minutes by means of a water aspirator. To the resulting product was added 0.9 (0.010 equiv.) g. of 1,4-butanediol and the mixture stirred for 5 minutes and again degassed for 5 minutes. The white, viscous mass which resulted was placed into a Teflon-lined aluminum mold and heated in a press at 110° for 20 hours. The product was obtained as a white, sticky gum and was not further characterized. Similar attempts to extend and cure the fluorinated polyester using larger and smaller amounts of curing reagents gave essentially the same results.

7. Plasticizing MVE/TFE Copolymer

Five strips of molded film from polymer sample 241 were immersed in boiling Freon E-5, $C_3F_7O\,[CF(CF_3)CF_2O\,]_3CFHCF$.

Immersion Time (Min.)	% Wt. Gain	% E-5 Remaining After 13 Days at R.T.
1	43.4	24
2	63.6	39
3	49.4	31
5	67.4	34
10	79.4	34
		Av. 32.4%

The samples became cloudy after immersion and were changed from a slightly elastic film to a highly elastic film.

B. Synthesis

1. $(CF_3O)_2CHCF_2Cl$

Into an evacuated 460 ml. steel cylinder equipped with a maximum indicating pressure gauge was condensed 284 mM of CF_3OF (est. purity 50 to 70%). The upper part of the cylinder was cooled with liquid N_2 and 25.8 mM of $CF_3OCH{=}CFCl$ (b. 85-87°; 97% cis-trans mixt.) was added slowly. The reactor was sealed, placed behind a barricade and allowed to warm slowly until reaction had occurred (approximately 15 to 30 min. as indicated by a pressure surge). The reaction was repeated until 129 mM of olefin had been reacted. In this manner approximately 90 g. of crude $(CF_3O)_2CHCF_2Cl$/ $CF_3OCHFCFClOCF_3$ was prepared during this period. In this preparation only a trace amount of telomeric products was noted.

Structural assignments of several of the precursors in the preparation of PVM and the isomeric compound $CF_3OCHFCFClOCF_3$ (infrared spectrum of this compound is shown in Figure 13) are confirmed by the NMR data in Table VII.

TABLE VII

NMR Data for Some Precursors[a] in the Preparation of PVM

Designation	Chemical Shift	Pattern and Splitting cps	Rel. Area	Assignment
		$CF_3OCHClCFCl_2$		
H	ca 4.4 tau	2° x ca 5	1	CHCl
F-A	-22.3 ppm	2° x 11	3.0	CF_3O
B	-7.8	4° x 11.0; 2° x 5.5	0.9	$CFCl_2$
		CF_3OCCl_2CHFCl		
H	+4.12 tau	2° x 48.1	-	CHFCl
Fa	-23.2 ppm	1°	2.96	CF_3O
Fb	+61.3 ppm	2° x 48.0	1.00	CHFCl

TABLE VII
(continued)

NMR Data for Some Precursors[a] in the Preparation of PVM

Designation	Chemical Shift	Pattern and Splitting cps	Rel. Area	Assignment
		$CF_3OCH=CFCl$ (cis to F)		
H	+3.65 tau	1°	-	OCH=
Fa	-14.0 ppm	1°	3.03	CF_3O-
Fb	+36.3 ppm	1°	1.00	=CFCl
		$CF_3OCH=CFCl$ (H trans to F)		
H	+4.30 tau	2° x 13.3	-	OCH=
Fa	-13.9 ppm	2° x 1.7	2.97	CF_3O-
Fb	+17.1 ppm	2° x 13.3, 4° x 1.6	1.00	=CFCl
		$CF_3OCHFCFClOCF_3$		
H-A	4.6 tau	2° x 54.5, 2° x 3.0		CHF
F-A	-21.1 ppm	2° x 9.6		CF_3O
B	-15.5	2° x 3.8		CF_3O
C	+2.9	two superimposable multiplets, each approx. 5° x 10, 2° x 3		CFCl
Da	+65.4	2° x 55, 4° x 4.3, 2° x 10.5		CHF in one isomer
Db	+66.4	2° x 55, 4° x 4.3, 2° x 10.5		CFH in other isomer

Peak D looks like a triplet.

(a) Infrared spectra of the first four compounds and NMR data for $(CF_3O)_2CHCF_2Cl$, $(CF_3O)_2C=CF_2$ were reported in the Second Annual Report.

2. Dehydrohalogenation of $(CF_3O)_2CHCF_2Cl$

a. KOH/Nujol

Into a 3-neck 250-ml. flask fitted with an ice water cooled condenser, a mechanical stirrer and a dropping funnel was placed 71 g. (3.1 moles) of powdered KOH and 100 ml. of Nujol. The mixture was heated to 150° and, while rapidly stirring, 30 g. of $(CF_3O)_2CHCF_2Cl$ (GLC analysis indicated 81% 1,1 adduct and 8.6% $CF_3OCHFCFClOCF_3$) was slowly added. The volatile dehydrohalogenation product was collected in a dry ice-acetone cooled trap. The crude product obtained, 14 g., was shown by GLC analysis to be 67.4% $(CF_3O)_2C=CF_2$, 5.7% of a mixture of $CF_3OCF=CFCl$ and $CF_3OCCl=CF_2$ and 16.7% starting material.

b. Solid KOH

Into a system similar to that described above was placed approximately 60 g. of KOH. The KOH was dried under vacuum for 16 hours at 90°. While stirring, 17.5 g. of adduct [65% $(CF_3O)_2CHCF_2Cl$ and 15% $CF_3OCHFCFClOCF_3$] was added slowly. The reaction was continued until reflux ceased (about 1/2 hour). The total crude yield was 3 g.

The combined products from several small runs (36 g.) was distilled through a 300 mm. vacuum-jacketed column packed with 1/8" stainless steel saddles. The major fraction, 17.9 g., boiled at 13-14° (b.p. of PVM by P-T measurements 11.9°). GLC analysis showed this fraction to be composed of 78% PVM, 12% of a mixture of $CF_3OCF=CFCl$ and $CF_3OCCl=CF_2$, 6.8% cis and trans $CF_3OCH=CFCl$ and trace amounts of additional impurities. Subsequent preparations had similar composition.

3. Attempted Alternate Synthesis of PVM

a. Reaction of CF_3OF with $HC\equiv CCOOH$

To a 100-ml. capacity Monel cylinder equipped with a pressure gage was added 1.4 g. (20 mM) of $HC\equiv CCOOH$. The cylinder was evacuated, cooled in liquid N_2 and 80 mM (approximately 50% pure) CF_3OF was added in incremental amounts. The cylinder was warmed to room temperature after each of three additions. Gage pressure at RT was 207 psi. After 24 hours the pressure remained the same and 75 mM of the CF_3OF mixture was recovered. After again adding the CF_3OF and heating the reaction mixture to 105°, about 75 mM of volatiles were again recovered. A black solid remained in the cylinder. An infrared spectrum of this material showed two broad maxima at about 3 and 5.8μ and no triple bond absorption at 4.7μ.

Although the triple bond absorption is absent in the solid reaction product and the infrared spectrum indicates the presence of a carboxyl group, the recovery of almost all of the CF_3OF would indicate polymerization rather than addition had occurred.

b. Reaction of CF_3OF with $HC{\equiv}CCOCl$

(1) Into an evacuated 700-ml. capacity steel cylinder fitted with a pressure gage was condensed 3.2 mM of $HC{\equiv}CCOCl$ (about 73% $HC{\equiv}CCOCl$ and 27% $POCl_3$) and 12.6 mM of CF_3OF (about 70% pure). The CF_3OF was added in small incremental amounts and the reactants were warmed to room temperature after each addition.

After the final addition of CF_3OF an infrared spectrum of the over-gases showed the presence of CO_2, COF_2, $POCl_3$, $HC{\equiv}CCOCl$ and a product exhibiting an absorption maximum at 5.47μ. A total of 9.2 mM of volatiles were recovered. A viscous oil remained in the cylinder. No further characterization was attempted.

(2) A second reaction was run at low pressure (100 mm. Hg or less) directly on a calibrated vacuum system.

No violent reaction occurred when 0.6 mM each of $HC{\equiv}CCOCl$ and CF_3OF were condensed into a trap on the vacuum system and allowed to warm to room temperature. A small amount of liquid product was obtained in this way which contained, in addition to $HC{\equiv}CCOCl$, a product or products which exhibited absorption maxima at 5.47 and 6.19μ. On standing, this material changed to a viscous brown material which was not further characterized.

(3) Into an evacuated 100-ml. capacity Fischer-Porter aerosol compatibility tube, fitted with a pressure gage, was condensed 7 g. of $HC{\equiv}CCOCl$ (∿73%) and 3.4 mM of CF_3OF (70%). The mixture was warmed to room temperature and at this temperature the gage pressure was 80 psig. The mixture was refrozen, 4.2 mM of CF_3OF was added, and the mixture again warmed to room temperature. The liquid in the tube was dark yellow and the pressure was 120 psig. When refreezing the reaction tube in liquid N_2 the reactants exploded.

4. $R_fOCF{=}CF_2$

a. $CF_3\overline{CFCF_2O}^{30}$

To a 5-neck, 3 l. flask, equipped with a mechanical stirrer, a low temperature reflux condenser, thermometer and a gas inlet tube was added

(30) F. C. McGrew, Brit. Pat. 943,373(1963).

84 g. (1.5 moles) of KOH, 140 ml. H_2O and 1000 ml. CH_3OH. The system was cooled to -53° and 136 g. (4.0 moles) of 50% H_2O_2 was slowly added. To this reaction mixture was added 116 g. (0.775 moles) of $CF_3CF{=}CF_2$ as a liquid at -78°. The temperature of the reactants dropped to -70° on addition of the propylene and the mixture changed to an ice slurry.

The bath temperature was slowly raised and at -35° a very vigorous reflux started. The mixture was maintained at about -40° and refluxed at this temperature for 1.5 hours. The reflux condenser, connected to a trap at -78°, and the reaction flask were allowed to warm at room temperature overnight and 55 g. of crude product was collected. GLC analysis (40' column) showed two major peaks of 47 and 53%. Infrared analysis showed minor peak to be the desired $CF_3\overline{CFCF_2O}$. An infrared spectrum of this compound is shown in Figure 14.

b. Reaction of CF_3COF with CsF

To a 100-ml. capacity Fischer-Porter aerosol compatibility tube fitted with a pressure gage was added 10 g. (65.8 mM) of anhydrous CsF and 10 ml. of diglyme (dist. from MaH_2). The reaction mixture was cooled to -196°, evacuated and 7.85 g. (47.3 mM) of CF_3COF was added. The reaction mixture was warmed to room temperature and shaken until the pressure remained constant (29 psig.). The reactor was reopened to the vacuum system and 24.4 mM of unreacted CF_3COF removed.

The reaction product was not isolated but reacted with 13.6 mM of $CF_3\overline{CFCF_2O}$ to give $C_2F_5OCF(CF_3)COF$. The amount of acid fluoride obtained was not determined.

c. $C_2F_5OCF(CF_3)COF$

Initial attempts to prepare these compounds were carried out using catalytic amounts of "Darco" activated carbon or CsF following the method outlined by Fritz, Moore and Selman.[31]

In a typical preparation 9 g. of 10% CsF on Darco carbon black was placed in a 300-ml. Monel cylinder. The cylinder was heated to red heat for about 15 minutes. The reactor was cooled to -196° and 166 mM of CF_3COF and 166 mM $CF_3\overline{CFCF_2O}$ (contg. about 20% $CF_3CF{=}CF_2$) was added. The cylinder was sealed, then heated to 55° for 96 hours. At the end of this time 19 g. of material having a vapor pressure of less than 1 atm. at room temperature was separated by trap to trap distillation. Other experiments are summarized in Table VII.

(31) See Reference No. 17

TABLE VIII

Reaction of R_fCOF with $CF_3\overline{CFCF_2O}$

Exp. No.[a]	R_f	(mM) $CF_3\overline{CFCF_2O}$[b]/mM R_fCOF	Reaction Temp. °C	Pressure at T psi	Time at T	Catalyst[c]	Wt. of Crude Product[d]
C	CF_3	52.5/52.5	-15	-	12	3 g. C	None
D	CF_3	166/166	-15	-	40	3 g. C	None
E	CF_3	166/166	-15	-	60	10 g. C	None
G	CF_3	166/166	-15	60	24	9 g. (10% CsF on C)	None
H	CF_3	166/166	RT	-	24	9 g. (10% CsF on C)	2 to 3
K,L	CF_3	166/166	55°	400	96	9 g. (10% CsF on C)	19
I	C_3F_7	52.5/52.5	RT	80	24	5 g. CsF	2-3
J	C_3F_7	52.5/52.5	92-105	320-500	44	5 g. CsF	5-7
N	CF_3	139/173	128	600	48	5 g. CsF +28 ml. diglyme	7
		(Distilled K, L and N)					11 g. pure adduct, b.p. 29.5-31.5°
4B	CF_3	211/336	75	600+	120	CsF in diglyme	11 g. pure adduct[e]
4C	CF_3	500/1000	75	390	120	CsF in diglyme	
4D	CF_3	370/573	75	300	120	CsF in diglyme	

(a) Monel cylinders, C, I, J, 4B 90 ml.; 4D 700 ml.; others 300 ml.
(b) Propylene oxide contained 10 to 20 mole % $CF_3CF=CF_2$.
(c) C was Darco activated carbon heated to red heat under vacuum. CsF dried at 150°+ under vacuum.
(d) Crude product separated by trap to trap distillation; material having a vapor pressure less than 1 amp. at RT.
(e) Fore-cut and after-cut contained high proportions of adduct.

Higher yields of adduct were obtained using much larger amounts of CsF. Thus, 100 grams of anhydrous CsF and 100 ml. of diglyme (dist. from CaH_2) were placed in a 2000 ml. steel cylinder and the cylinder evacuated. The mixture was cooled to -196° and 86 g. (740 mM) CF_3COF was added. The cylinder valve was closed and the cylinder was shaken, while warming to room temperature, until a minimum pressure was attained. The reaction mixture was again cooled to -196° and 122 g. $CF_3\overline{CFCF_2O}$ (purity 80-90 mole % epoxide, remainder mostly $CF_3CF=CF_2$) was added. The cylinder valve was closed and the cylinder warmed to room temperature. Reaction occurred on warming and shaking, as evidenced by an exotherm. Shaking was continued until the pressure dropped to zero.

The reaction product was transferred to a vacuum system and a crude product separation was effected by trap to trap distillation, which yielded 84 g. of material having a vapor pressure greater than 600 mm. and 113 g. of material with a vapor pressure less than 600 mm.

The combined products from several runs, 446 g., distilled on a 150 cm. packed column gave as a major cut 297 g. of material boiling at 27 to 30°. Chromatographic analysis (16' column) indicated 98% $+C_2F_5OCF(CF_3)COF$. Chromatographic analysis using a 24' column (HMDS chromosorb with dinonyl phthalate as the stationary phase, at RT) separated the major product peak into two and possibly a third component. The resolution was only fair, permitting only an estimate of product purity at about 85% $C_2F_5OCF(CF_3)COF$. (Infrared Spectrum, Figure 15.) The minor component exhibited an infrared absorption maximum at 5.62μ. This component is presumed to be methyl isopropyl ketone, $CF_3COCF(CF_3)_2$, which is a reaction product of CF_3COF with an impurity (C_3F_6) present.

An additional distillation cut, 34.4 g., boiling between 52 and 56°, was analyzed chromatographically (Kel-F ester on HMDS chromosorb) and was found to contain two components in an area ratio of 78/22. The minor component was identified as ethyl esopropyl ketone, $C_2F_5COCF(CF_3)_2$, by comparing its infrared spectrum with that of an authentic sample (Figure 16). The larger component was identified as $C_3F_7OCF(CF_3)COF$ by comparing its infrared spectrum (Figure 17) with the maxima reported by Moore, et al.[32] for this compound.

NMR analysis on a GLC pure product confirms the structure of the major adduct as $C_2F_5OCF(CF_3)COF$.

(32) E. P. Moore, Jr., A. S. Milian, Jr., H. S. Eleuterio, Fr. Pat. 1,275,799 (2 Oct. 1961).

NMR Analysis of $C_2F_5OCF(CF_3)COF$

Designation	Chemical Shift ppm	Pattern and Splitting cps	Rel. Area	Assignment
A	-101.5		2.5	COF
B	+ 6.7		9.0	CF_3
D	+ 11.3		9.1	CF_3
G	+ 54.7		2.5	CF
B', C, E, F	+ 8.15, + 15.55	(Non equivalent quartet)	5.4	CF_2

d. $C_3F_7OCF(CF_3)COF$

Similar to the above procedure 76.5 g. (470 mM) of C_2F_5COF and 70 g. CF_3CFCF_2O were reacted, in diglyme in the presence of 100 g. of CsF, to give 124.5 g. of material having a vapor pressure less than 600 mm. Distillation of the product from two runs, 246.5 g. gave 122 g. of material boiling at 48 to 53°. Chromatographic analysis of this cut (16' column) indicated one major and two minor components in the ratio of 5.1:8. 9:86 (in the order of retention times). The major component is identified as $C_3F_7OCF(CF_3)COF$ by comparison of its infrared spectrum with that of the previously identified by-product in the preparation of $C_2F_5OCF(CF_3)COF$ and by the following NMR analysis. Chemical shifts for fluorine are given with respect to $CF_2ClCFCl_2$ solvent and COF given with respect to CF_3COOH.

NMR Data for $C_3F_7OCF(CF_3)COF$

Designation	Chemical Shift ppm	Pattern and Splitting cps	Rel. Area	Assignment
A	-103.1	Multiplet	1.0	COF
B, C, F, G	+ 2.39, + 11.8	Nonequivalence quartet with further splitting	2.0	OCF_2
D	+ 4.68	3°	3.2	CF_3 on CF_2

NMR Data for $C_3F_7OCF(CF_3)COF$
(continued)

Designation	Chemical Shift ppm	Pattern and Splitting cps	Rel. Area	Assignment
E	+ 5.27	2° x 5.6, 2° x 3.1	3.4	CF_3 on CF
H	+52.7	Barely resolvable triplet	2.3	CF_2
I	+53.5	Broad doublet	0.9	CF

e. $R_fOCF(CF_3)COONa$

To a one-liter capacity, vented poly(ethylene) bottle, fitted with dropping funnel, was added 192 g. of H_2O. While stirring, 12 g. (227 mM) of $C_2F_5OCF(CF_3)COF$ was added slowly. The immiscible acid fluoride formed a second layer. While stirring, over a period of 30 minutes, the acid fluoride gradually hydrolyzed and went into solution, resulting in only a slight exotherm.

The acid solution was neutralized to a phenolphthalein end point and the water removed under reduced pressure at about 50° yielding 56 g. of a slightly pink solid which melted with decomposition. An infrared spectrum of this compound is shown in Figure 18.

Similarly prepared was $C_3F_7OCF(CF_3)COONa$. An infrared spectrum of this compound is shown in Figure 19.

f. Decarboxylation of $R_fOCF(CF_3)COONa$

Into a one-liter, round bottom flask, attached to a vacuum system, was placed 56 g. of $C_2F_5OCF(CF_3)COONa$/NaF mixture (as prepared from neutralization of the acid fluoride). The system was evacuated and the salt heated with a direct flame such that a steady gas evolution was maintained. The volatile pyrolysis products were collected in a liquid N_2 cooled finger trap. When the salt was totally pyrolyzed (no evolution of gas), 38 g. of crude product was collected. GLC analysis (16" Kel-F ester on HMDS chromosorb column at RT) and infrared analysis showed the product contained four components. The GLC areas were 37% CO_2, 59% $C_2F_5OCF{=}CF_2$, 1.3% $C_2F_5OCF(CF_3)COF$ and 2.7% of an unidentified compound showing no infrared $C{=}C$ absorption. The main component was separated by GLC and a vapor density molecular weight was found to be 200 g./mole (calc. for C_4F_8O, 216 g. (mole). The following NMR data supports the structural assignment of $C_2F_5OCF{=}CF_2$.

$C_2F_5OCF=CF_2$

Designation	Chemical Shift ppm	Pattern and Splitting cps	Rel. Area	Assignment
A	+ 11.4	Multiplet	3.00	CF_3
B	+ 15.3	Multiplet	2.02	CF_2
C	+ 40.8	2° x 88.0, 2° x 66.1	0.98	F trans to O
D	+ 48.0	2° x 111.2, 2° x 88.0 3° x 5.67	0.94	F cis to O
E	+ 61.1	2° x 110.9, 2° x 65.6 3° x 6.0	0.88	F gen to O

An infrared spectrum of this compound is shown in Figure 20.

Similarly prepared was $C_3F_7OCF=CF_2$. An infrared spectrum of this compound is shown in Figure 21 and the following NMR data support the structure assigned this compound.

$C_3F_7OCF=CF_2$

Designation	Chemical Shift ppm	Pattern and Splitting cps	Rel. Area	Assignment
A	TFAA +6.4 ppm	3° x 7.8	3.0	CF_3
B	+10.6	2° x 7.7	2.0	CF_2-O
C	+40.3	2° x 86, 2° x 65	1.1	=CF trans to O
D	+47.6	2° x 86, 2° x 110 3° x 27	1.1	=CF cis to O
E	+54.2	Singlet	2.0	CF_2 on CF_3
F	+60.4	2° x 65, 2° x 110 3° x 27	1.0	=CF gem to O

5. Attempted Preparation of $R_fOCF(CF_3)COF$

a. Gamma Ray Irradiation of $CF_3CF=CF_2$, O_2, and C_3F_7COF

Into an evacuated 13 ml. capacity Carius tube, at -196°, was condensed 7 mM each of $CF_3CF=CF_2$, O_2, and C_3F_7COF. (The O_2 had a vapor pressure of 160 mm. at liquid N temperature.)

The ampule was placed 1.91 cm. from the Co^{60} source (radiation flux 7×10^5 r/hr). After a total dose of 5.1×10^6 Rep., approximately 16.1 mM of volatiles were removed which contained, in addition to the original reactants, $CF_3\overset{\frown}{CFCF_2}O$. Remaining in the ampule was a high boiling product which had a vapor pressure of less than 5 mm. at RT.

An infrared spectrum of the high boiling product indicated the presence of COOH (broad at 3.2μ) and COF (strong at 5.3μ). In addition, other maxima were found at 5.63, 8.1, 9.05, 9.9, 10.3 and 10.72μ. None of these correspond to either C_3F_7COF or C_3F_7COOH. The spectrum is poorly resolved between 7.6 and 9.5μ. The reported[32] major IR maxima for $C_3F_7OCF(CF_3)COF$ are 5.3, 7.4, 7.5, 8.6, 8.8, 9.0, 9.8 and 10.0μ.

b. U. V. Irradiation of $CF_3CF=CF_2$, O_2, and CF_3COF

To an evacuated 12-liter, 3-neck flask, fitted with a monometer, quartz u.v. immersion well and gas charging valve, was added 118 mM $CF_3CF=CF_2$, 118 mM O_2, and 236 mM CF_3COF. The reactants were irradiated at room temperature with a Hanovia 8A36 high pressure quartz mercury-vapor lamp. After one hour irradiation the pressure dropped from 735 mm. to 616 mm. On continued irradiation for a total of 17 hours the final pressure was 547 mm. Trap to trap distillation gave 8-9 g. of material having a vapor pressure of less than 1 atm. at room temperature. An infrared spectrum of this product showed maxima at 2.8(w), 5.25(s), 5.49(w), 5.60(w), 7.6, 8.0, 9.3μ.

6. Attempted Preparation of $CF_3OCF=CFOCF_3$

a. $CF_3OCCl_2CFCl_2$

To a 700 ml. capacity steel cylinder, equipped with a pressure gage, was added 25 g. (152 mM) of C_2Cl_4. The cylinder was cooled to -196° and CF_3OF was added in small amounts ranging initially from 6.9 mM to a final addition of 69 mM. The cylinder was placed behind a barricade and warmed to room temperature after each CF_3OF addition. After a total of 298 mM of CF_3OF was added, the reaction product was collected by venting the cylinder through a trap cooled to -78°. The crude material from two

similar runs was washed with aqueous KI solution and rectified on a 36 plate spinning band column yielding 45.7 g. of $CF_3OCCl_2CFCl_2$, b.p. 110°. An infrared spectrum of this compound is shown in Figure 22 and supporting NMR data is given below. Chemical shift for fluorine are given with respect to external CF_3COOH.

$CF_3OCCl_2CFCl_2$

Designation	Chemical Shift ppm	Pattern and Splitting cps	Rel. Area	Assignment
A	-23.6	Singlet	3.05	CF_3O
B	-11.7	Singlet	1.00	$CFCl_2$

b. $CF_3OCCl=CFCl$

To a one-liter, 3-neck flask, fitted with an addition funnel and a Vigreaux distillation column, was added 104 g. (1.6 moles) of zinc dust and 250 ml. of freshly distilled dioxane. The zinc was activated by the addition of a few crystals of $ZnCl_2$ and by the addition of a trace of gaseous HBr. The reaction mixture was heated to reflux and 119 g (1.0 moles) of $CF_3OCCl_2CFCl_2$ was added. The rate of addition was governed by the reflux temperature and the dechlorinated product was removed as formed over a temperature range of 50 to 92° yielding 106 g. of crude $CF_3OCCl=CFCl$. Fractionation of 120 g. of combined crude product on a 36 plate spinning band column gave 69 g. of $CF_3OCCl=CFCl$ as a 60/40 cis/trans mixture, b.p.51°; d_4^{20}, 1.533; n_D^{20}, 1.3420. An infrared spectrum of the 60/40 cis/trans mixture of $CF_3OCCl=CFCl$ is shown in Figure 23 and supporting NMR data is given below. Chemical shifts for fluorine are given with respect to external CF_3COOH.

$CF_3OCCl=CFCl$

Designation	Chemical Shift ppm	Pattern and Splitting cps	Rel. Area	Assignment
A	-17.5	Singlet	3.00	CF_3O
B	-16.9	2° x 4.8	2.08	CF_3O
C	+11.9	4° x 4.6	0.75	=CFCl
D	+18.6	Singlet	1.04	=CFCl

Peaks A and D appear to belong to the isomer in which the two Cl atoms are trans to one another and peaks B and C to the cis isomer.

c. $(CF_3O)_2CClCF_2Cl$ and $CF_3OCFClCFClOCF_3$

In a manner similar to the previous addition of CF_3OF, 60 g. of the cis, trans mixture of $CF_3OCCl=CFCl$ was reacted with CF_3OF to give 76 g. of crude adduct. Chromatographic analysis indicated 94% $(CF_3O)_2CClCF_2Cl$/ $CF_3OCFClCFClOCF_3$ in a molar ratio of 1/2.57, micro b.p. 78°. (Normal 8' GLC column showed a single peak; however, the two isomers were resolved on a 40' column and the molar ratio was substantiated by NMR analysis.) An infrared spectrum of each isomer is shown in Figures 24 and 25.

NMR Data for $(CF_3O)_2CClCF_2Cl$

Designation	Chemical Shift ppm	Pattern and Splitting cps	Rel. Area	Assignment
A	-22.5	3° x 3.7	8.1	CF_3O
C	- 6.9	7° x 3.6	1.7	CF_2Cl
		$CF_3OCFClCFClOCF_3$		
B	-21.5	2° x 10.9 plus other structure	19.1	CF_3O
D	+ 1.1	Complex multiplet	5.6	CFCl

7. Attempted Synthesis of $CF_2=CFC(OCF_3)=CF_2$

a. $\overline{CF_2CF_2CFClCCl}OCF_3$

Into a 460 ml. steel cylinder equipped with a pressure gauge was condensed 138 mM of a gas mixture containing about 70 mole % CF_3OF. The upper part of the cylinder was cooled to -186° and 13.8 mM of $\overline{CF_2CF_2CCl=CCl}$ was added. The cylinder was removed from the vacuum system and allowed to warm to room temperature behind a barricade. This procedure was repeated until 69.0 mM of the cycloolefin was added. The cycle was repeated until 414 mM of the cyclobutene and 908 mM of the CF_3OF mixture was reacted, yielding 84.5 g. of crude addition product. GLC analysis indicated the crude product to contain 76.5% $\overline{CF_2CF_2CFClCCl}OCF_3$ and 16.1% of the starting olefin.

The crude product was washed with aqueous KI solution and distilled through a spinning band column (35 theoretical plates) to give 60.6 g. (88% conversion) of product boiling at 85-87°. GLC analysis of the distillate indicated 96% $\overline{CF_2CF_2CFClCClOCF_3}$ and 4% $\overline{CF_2CF_2CCl{=}CCl}$. ($d^{20}$, 1.702; η_D^{20}, 1.3282 for 96/4 mixture.) A vapor density molecular weight was found to be 293 g./mole which is consistant with a 95/5 mixture of the adduct/olefin.

An infrared spectrum of this compound is shown in Figure 26 and NMR data is given below.

NMR Data for $\overline{CF_2CF_2CFClCClOCF_3}$

Designation	Chemical Shift ppm	Pattern and Splitting cps	Rel. Area	Assignment
A	-21.6	Multiplet	2.9	OCF_3
B-1	+38.4	Multiplet		
B-2	+42.1	Multiplet	2.0	Ring F's probably cis to Cl
C-1	+48.0	Multiplet		
C-1	+52.0	Multiplet		
C-3	+55.8	Multiplet	3.0	Other F's in CF_2's plus F in CFCl

b. Dechlorination of $\overline{CF_2CF_2CFClCClOCF_3}$

To a 150-ml., 3-neck flask fitted with a reflux condenser, addition funnel and mechanical stirrer was added 40 g. (0.61 moles) of zinc dust and 150 ml. of EtOH. The reaction mixture was heated to reflux and the zinc was activated with a trace of gaseous HBr. To this reaction mixture was added $\overline{CF_2CF_2CFClCClOCF_3}$, 92.6 g. (0.31 moles). A reaction occurred almost immediately and the low boiling product was collected in a dry-ice cooled trap connected to the condenser.

Fractionation of the reaction product through a 100-cm. column packed with 1/8 in. stainless steel helices, gave the following cuts:

Temperature °C	Amount g.	GLC indicated purity %
34-35°	12.7	93
35-38°	22.1	98+
Pot residue	7	Mainly olefinic product.

An infrared spectrum of this compound is shown in Figure 27 and NMR data is given below.

NMR Data for $\overline{CF_2CF_2CF=COCF_3}$

Designation	Chemical Shift ppm	Pattern and Splitting cps	Rel. Area	Assignment
A	-14.6	2° x 7.9 plus complex splitting	3.0	OCF_3
B	+39.7		0.2	Impurity
C	+44.1	2° x 10.5	4.2	CF_2
D	+51.0	Complex multiplet	1.0	=CF

c. Pyrolysis of $\overline{CF_2CF_2CF=COCF_3}$

Through an evacuated 1-inch diameter Vycor tube 15 inches long containing crushed Vycor was passed 12 g. of the cyclic olefin over a period of several hours. The olefin was added intermittantly at progressively higher temperatures, at about 15 mm. pressure. The pyrolyzate was collected in a liquid nitrogen cooled trap and the course of the reaction was followed by infrared analysis of the gases collected.

At 525° and at 625° the product contained mostly unreacted $\overline{CF_2CF_2CF=COCF_3}$ and a product showing a strong maximum at 5.80μ and a weak maximum at 5.5μ . The ratio of unreacted olefin to unidentified product was 91/9. (By GLC analysis, 16', RT, Kel-F ester on Chromosorb.) In addition, at 525° CO_2 was noted and at 625° COF_2 was noted. The total weight of material collected was only 3 g. and the reactor contained carbon.

There was insufficient product obtained for NMR analysis.

8. $CF_2=CFCOF$

a. $HOOCCF_2CF_2COOCH_3$

To a 100-ml., 3-neck flask fitted with an addition funnel, reflux condenser, and stirrer was added 10 g. (57 mM) of perfluorosuccinic anhydride. While stirring, 1.8 g. (57 mM) of CH_3OH was slowly added with the resultant exotherm controlled by the addition of alcohol. An infrared spectrum of the product is shown in Figure 28.

On standing, precipitation of $(CF_2)_2(COOH)_2$ was noted.

b. $CH_3OOCCF_2CF_2COONa$

The salt-ester was prepared by the addition of 0.5 N. NaOH to a methanolic solution of the ester-acid. Hydrolysis occurred rapidly at a pH only slightly above 7. An infrared spectrum of the salt-ester after drying and washing with Et_2O is shown in Figure 29.

c. Pyrolysis of $NaOOCCF_2CF_2COONa$

In an initial qualitative experiment crude $NaOOCCF_2CF_2COOCH_2CF_3$ was pyrolyzed and the pyrolysis products collected. An infrared spectrum of the volatile products showed CO_2 to be present and also a product which exhibited infrared absorption of approximately equal intensity at 5.39 and 5.73μ.

A more controlled pyrolysis of 7 g. of material, originally presumed to be $CF_3CH_2OOCCF_2CF_2COONa$, but subsequently found to be mostly the disodium salt (0.029 moles), was carried out on a closed evacuated system. The dried salt mixture, 7.0 g., was intimately mixed with 1/8 inch diameter copper shot and placed in a 100-ml., one-neck flask and the flask evacuated. The flask was slowly heated to progressively higher temperatures and at 305° a steady, slow evolution of gas was noted. The flask temperature was maintained at 305 to 320° until gas evolution ceased. Infrared and GLC analysis (40' column) showed two main products, CO_2 and $CF_2=CFCOF$. A crude trap-to-trap separation of the two products gave 0.029 moles of low boiling gases (presumed to be mostly CO_2) and 1.3 g. of crude $CF_2=CFCOF$. An infrared spectrum of $CF_2=CFCOF$ is shown in Figure 30 and NMR data is given below.

NMR Data for CF_2=CFCOF

Designation	Chemical Shift ppm	Pattern and Splitting cps	Rel. Area	Assignment
H	Broad series of peaks from approx. 4 to 8 tau			Dipentene Inhibitor.
Fa	-97.3	2°, 2°, 2°	29.7	COF
Fb	+ 0.7	2°, 2°, 2°	29.5	F trans to COF
Fc	+13.7	2°, 2°, 2°	29.8	F cis to COF
Fd	+110.3	2°, 2°, 2°	30.7	F gem to COF

An infrared spectrum of the pyrolyzate of $CH_3OOCCF_2CF_2COONa$, as prepared above, also indicated the presence of CF_2=CFCOF.

9. Dehydration of $CF_3CHO \cdot H_2O$

To a 300-ml., 3-neck flask, equipped with a mechanical stirrer, dropping funnel and an ice-cooled condenser, was added about 100 g. of $P_2O_5 \cdot CF_3CHO \cdot H_2O$, 20 g., was added dropwise to the P_2O_5. An immediate reaction occurred and the volatile CF_3CHO, b.p. -19°, was collected in a dry-ice cooled trap. The crude yield was 5 g. and an infrared spectrum showed all the maxima consistent with CF_3CHO and two additional maxima at 4.3 and 4.85μ. (The crude aldehyde was used in polymer samples 251 and 255, Table V.) The dehydrated aldehyde spontaneously polymerized when stored overnight in a steel cylinder at room temperature.

Subsequent preparations gave CF_3CHO which was indicated by GLC analysis (40' column) to contain no impurity.

10. HC≡CCOCL

Into a one-liter, 2-neck flask fitted with a pressure compensated addition funnel, containing 70 g. (1 mole) of HC≡CCOOH, was added 209 g. (1 mole) of PCl_5. The flask was fitted with a gas outlet tube connected to a finger trap cooled to -196° and the entire system was evacuated.

The acid was added dropwise with an immediate reaction occurring and the crude product, 73 g., was collected in the finger trap as formed. The product was a colorless liquid which GLC analysis (16', silicone grease on Haloport at 87°) indicated to be a mixture of 73% HC≡CCOCl and 27%

$POCl_3$. An infrared spectrum of the acid chloride is shown in Figure 31.

11. Reaction of C_2F_5COOH with FSO_3H

Into a 250-ml., 3-neck flask equipped with a dropping funnel, a magnetic stirring bar and condenser was added 105 ml. of FSO_3H. The acid was heated to reflux and 120 g. C_2F_5COOH was added over a period of 2 to 3 hours and the low boiling product collected in a LOX cooled trap connected to the condenser. A GLC analysis of the crude product, 40.3 g., (16', Kel-F ester on Chromosorb), indicated only a trace of impurity but an infrared spectrum showed, in addition to the product maxima (of C_2F_5COF), a strong maximum at 9.7μ(SiF_4) and a weak minimum at 5.48μ.

12. Hydrolytic Stability of $CF_3OCF=CF_2$ and $(CF_3O)_2C=CF_2$

Into a 3-cc. capacity Pyrex ampule was added 27 mM of H_2O. The ampule was cooled in liquid N_2, evacuated and the water degassed by repeated freezing and warming. GLC pure $CF_3OCF=CF_2$ (1.08 mM) was added and the ampule sealed. After 21 days contact at room temperature the ampule was reopened to the vacuum system and essentially all of the vinyl ether recovered. An IR spectrum of the recovered ether showed only two very minor changes, very weak maxima at 6.7 and 9.9μ. There was no indication of the presence of CO_2.

Using the above procedure, $(CF_3O)_2C=CF_2$ was kept in contact with H_2O for 21 days. No indication of hydrolysis was observed.

13. Attempted Preparation of $(CF_3)_2CFOCF=CF_2$

A Fischer-Porter tube was charged with 30 ml. of diglyme (dried over $LiAlH_4$ and distilled from CaH_2) and 2.9 g. (0.05 mole) of KF (vac. dried overnight at 120° and redried on a hot plate prior to use). The mixture was then frozen in liquid O_2, the vessel evacuated, and 8.3 g. (0.05 mole) of hexafluoroacetone was condensed in. Upon warming to room temperature most, but not all, of the KF went into solution indicating formation of $(CF_3)_2CFOK$. After standing overnight at room temperature, the mixture was again frozen and 5 g. (0.05 mole) of $CF_2=CF_2$ was condensed in. Upon warming to room temperature, a pressure of 80 p.s.i. showed on the gage. After standing for 72 hours the pressure gage showed 25 p.s.i. and the reaction mixture had become yellow. The tube was then immersed in a water bath at 80° for four hours. Upon cooling to room temperature, some crystalline material formed in the reaction mixture and the pressure gage showed 15-18 p.s.i. The gasses were condensed into a liquid N_2 trap on the vacuum line with warming of the reaction vessel to insure transfer of all volatiles. Infrared

analysis of the condensed gases revealed the presence of only $CF_2=CF_2$. The gases were then passed through a cold trap held at-50 to -60° and into a liquid oxygen trap. The material caught in the -50 to -60° trap was analyzed by infrared and again no bands assignable to the desired product, perfluoro(vinyl isopropyl ether), were observed.

14. $\overline{CF_2CF_2S}_4$ (Perfluoro-1,2,3,4-tetrathiane)[33]

A one-liter, 3-neck flask was fitted with a 30-cm. x 25-mm. glass column wrapped with a Marsh beaded heater. The column was topped with an air-cooled straight distillation take-off leading by means of wide bore tubing into a dry ice-acetone cooled receiver. The receiver was in turn vented to the atmosphere through a liquid oxygen trap which was protected from moisture by means of a calcium chloride tube. The reaction flask was charged with 900 g. of sulfur and was heated by means of a heating mantle until the sulfur began to reflux. Through a gas inlet tube extending to just above the surface of the boiling suflur, 300 g. of tetrafluoroethylene was introduced over a 4-5 hour period. The column heater was adjusted so that the head temperature was maintained at 230-40° throughout the run. The mixture of viscous, yellow liquid and solid collected in the receiver was allowed to warm to ambient temperature during which time thiocarbonyl fluoride distilled off. The remaining liquid was distilled under vacuum using acid-washed equipment and a total take-off head, three fractions being collected as indicated below.

Fraction	B.P.	Press	Weight
WBN 27.22	40-42°	6-7 mm	64.4 g.
WBN 27.23	39-40°	4-5 mm	63.0 g.
WBN 27.24	38-39°	3-4 mm	32.0 g.

A considerable amount of material was lost during distillation through polymerization. The polymer is a yellow gummy substance which is readily attacked and dissolved by aqueous potassium hydroxide. All three fractions contained impurities as shown by V. P. C. analysis, but careful V. P. C. analysis could not be performed because of the tendency for the products to polymerize in the injection syringes. The fractions were, therefore, used for subsequent preparations of $ClSCF_2CF_2SCl$ without further purification.

(33) C. G. Krespan, U. S. Pat. 3,099,688.

15. $ClSCF_2CF_2SCl$ [1,1,2,2-tetrafluoroethane-1,2-bis(sulfenyl chloride)]

Chlorine was bubbled into a solution containing 90 g. of crude perfluoro-1,2,3,4-tetrathiane and 75° g. of chloroform (dried over $CaCl_2$ and freshly distilled) at room temperature for four hours. The resulting orange solution was then cooled to 0°, saturated with chlorine and allowed to stand for 18 hours. The solution was distilled to remove chloroform and SCl_2 until the pot temperature reached 160°. The residual liquid was then fractionally distilled through a 70-cm. column packed with glass rings to give a fraction (A) b.p. 46-8°/36 mm. and a fraction (B) b.p. 75-85°/36 mm. Fraction A was a yellow fuming liquid with an obnoxious odor. Fraction A could not be recovered after injection on several V.P.C. columns. NMR analysis of Fraction A showed a singlet at +10.1 ppm from trifluoroacetic acid standard. This is consistant with the structure $ClSCF_2CF_2SCl$. The infrared spectrum likewise was consistent with the assigned structure. Elemental analysis of Fraction A was high for sulfur and chlorine and low for carbon and fluorine, suggesting contamination by SCl_2. The yield of Fraction A was 15g.

NMR Data for $ClSCF_2CF_2SCl$

Designation	Chemical Shift ppm	Pattern Splitting cps	Assignment
F	+10.1	1°	CF_2

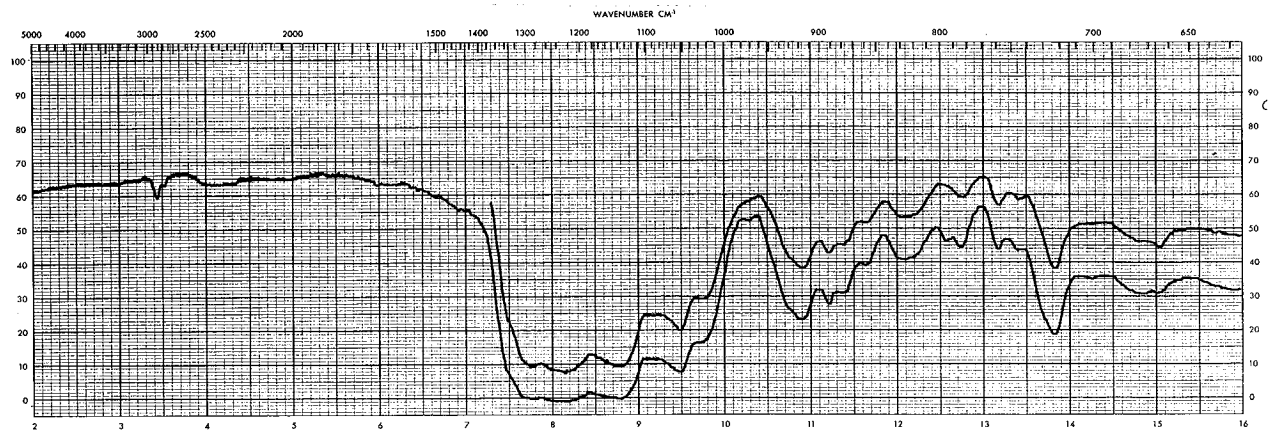


Figure 1. Infrared Spectrum of $CF_3NO/CF_3OCF{=}CF_2$ Copolymer (Freon 113 cast film)

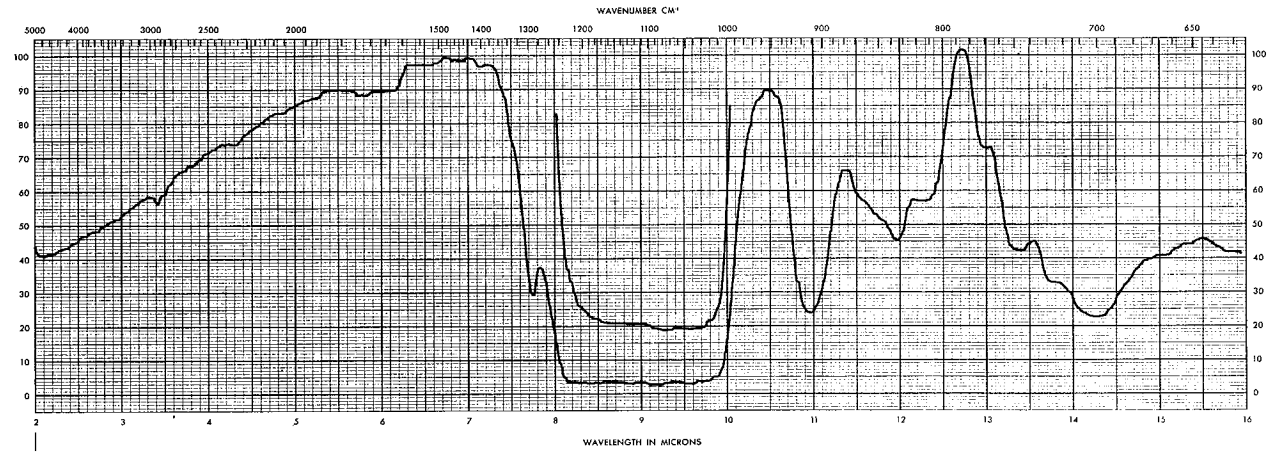


Figure 2. Infrared Spectrum of $CF_3NO/C_2F_5OCF{=}CF_2$ Copolymer (ATR, 3 Reflections, 53°)

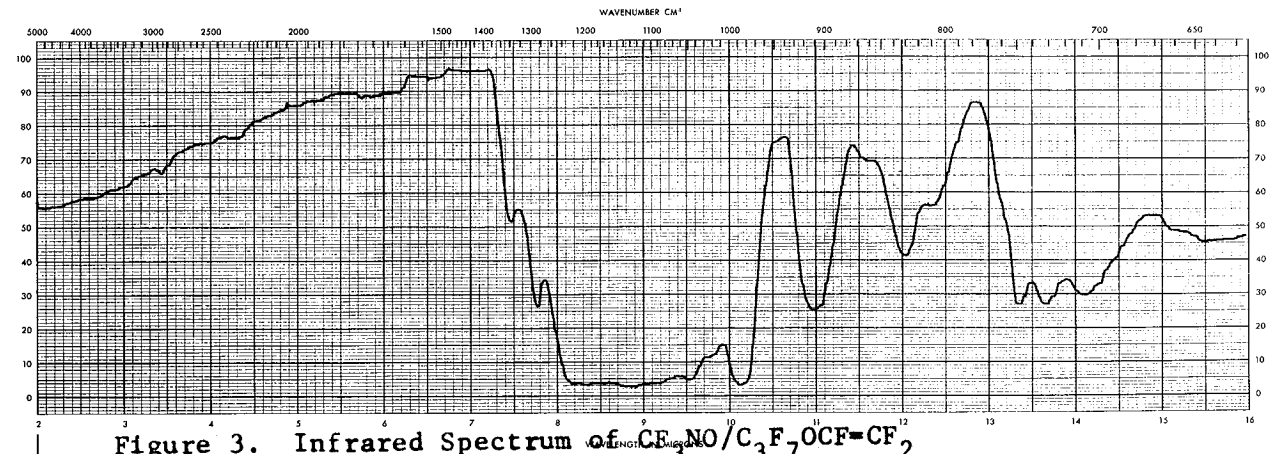


Figure 3. Infrared Spectrum of $CF_3NO/C_3F_7OCF{=}CF_2$ Copolymer (ATR, 3 Reflections, 54°)

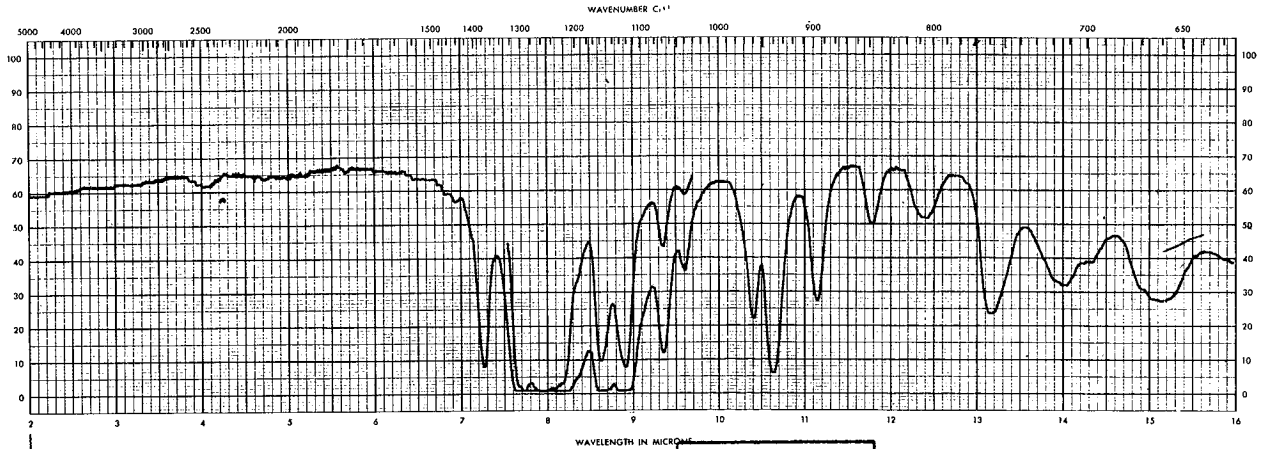


Figure 4. Infrared Spectrum of $CF_3NCF_2C(OCF_3)_2O$ (gas)

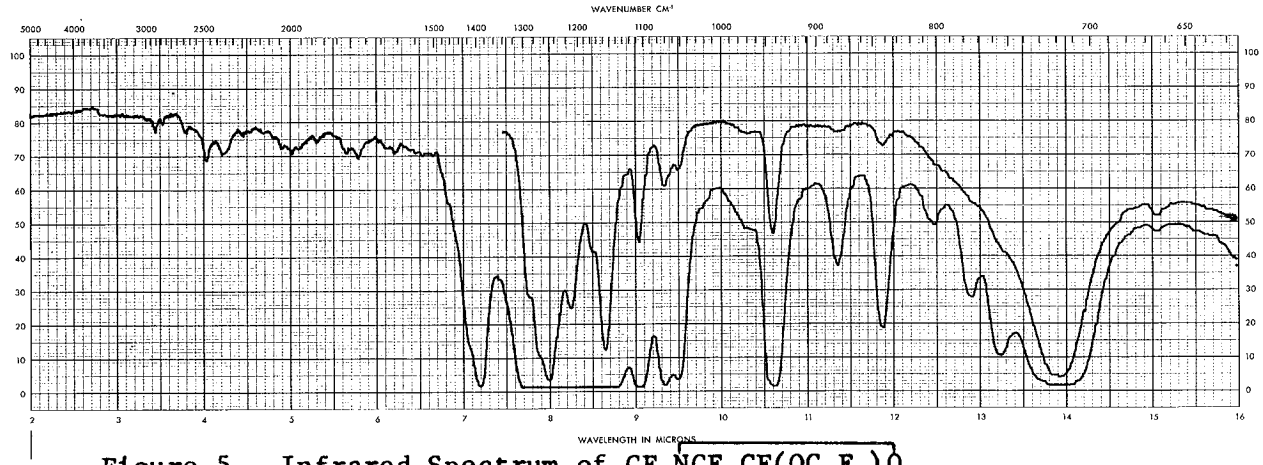


Figure 5. Infrared Spectrum of $CF_3NCF_2CF(OC_2F_5)O$ (gas, 3 and 35 mm.)

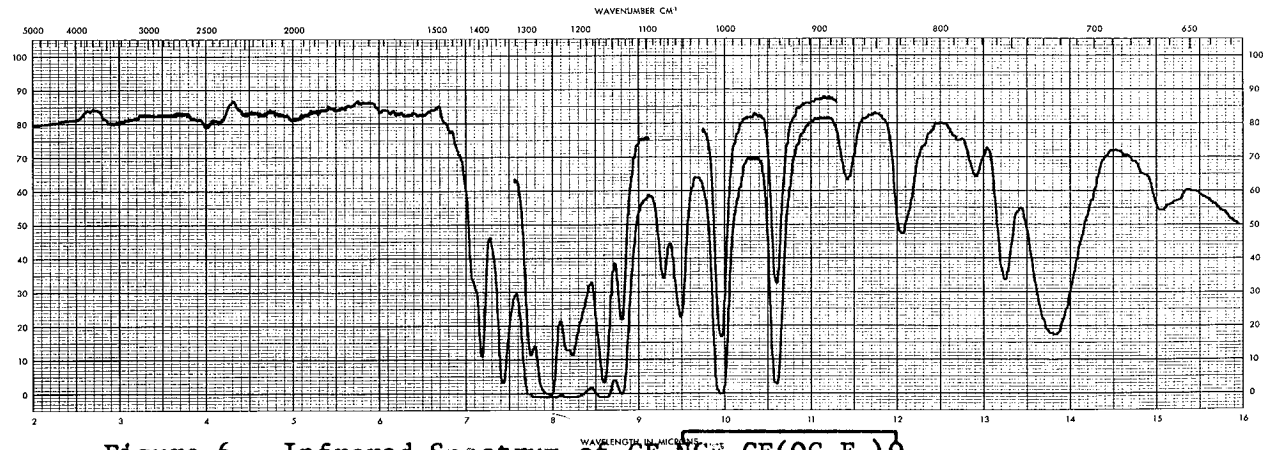


Figure 6. Infrared Spectrum of $CF_3NCF_2CF(OC_3F_7)O$ (gas, 12 and 36 mm.)

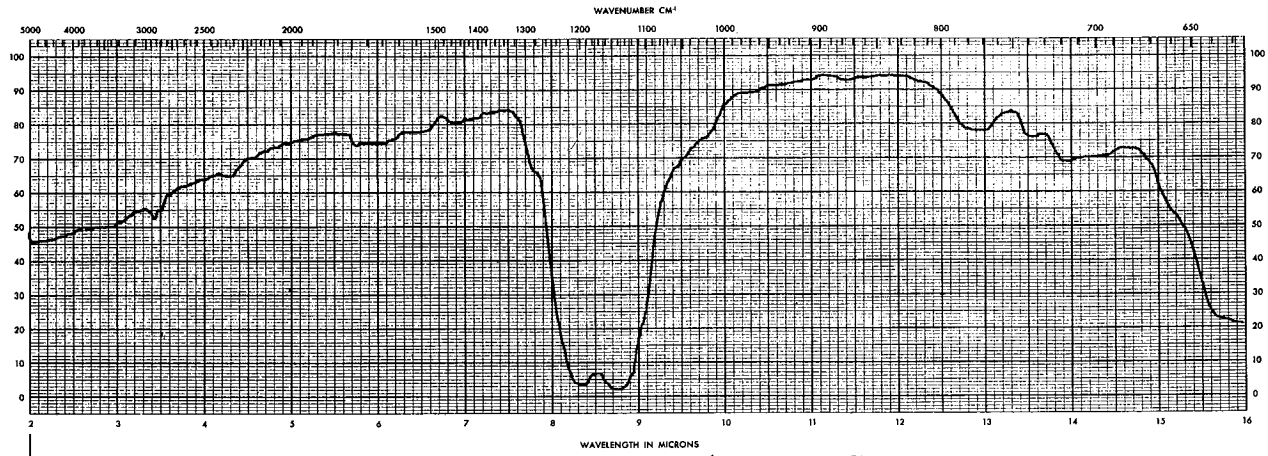


Figure 7. Infrared Spectrum of an 85/15 mole % $C_2F_4/(CF_3O)_2C=CF_2$ Copolymer (ATR, 3 Reflections, 59°)

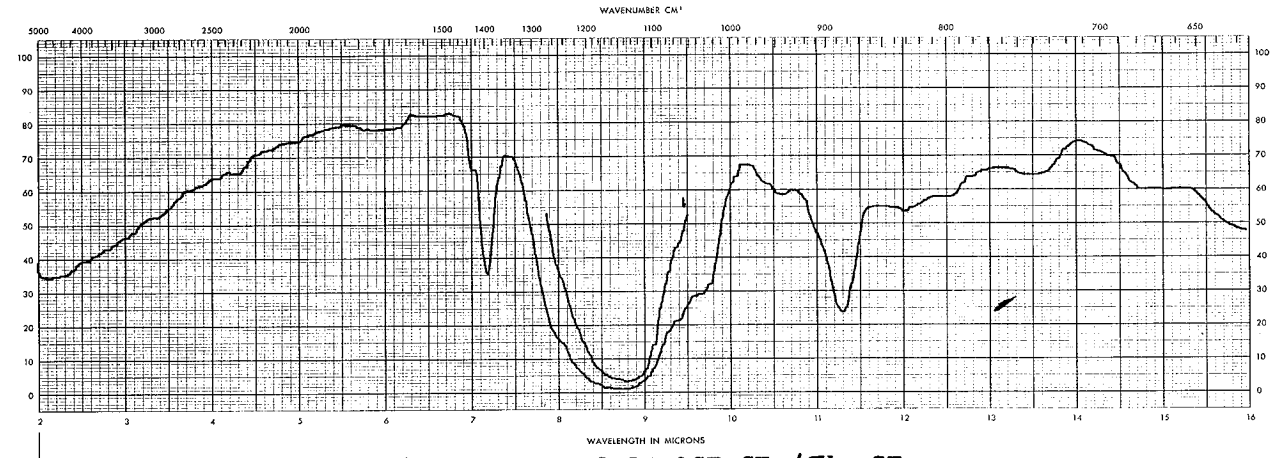


Figure 8. Infrared Spectrum of $CF_3OCF=CF_2/CH_2=CF_2$ Copolymer (ATR, 3 Reflections, 70°)

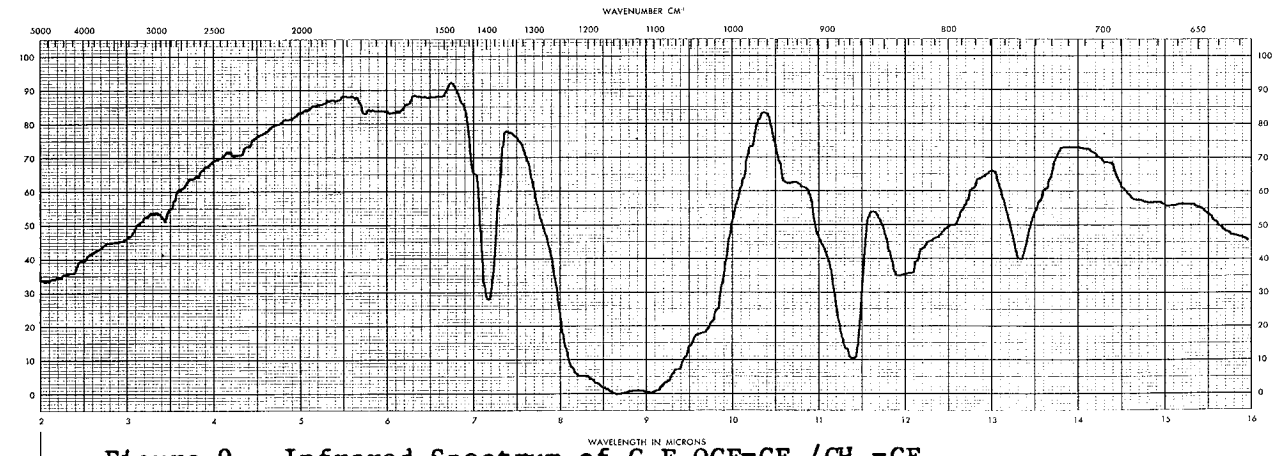


Figure 9. Infrared Spectrum of $C_2F_5OCF=CF_2/CH_2=CF_2$ Copolymer (ATR, 3 Reflections, 56°)

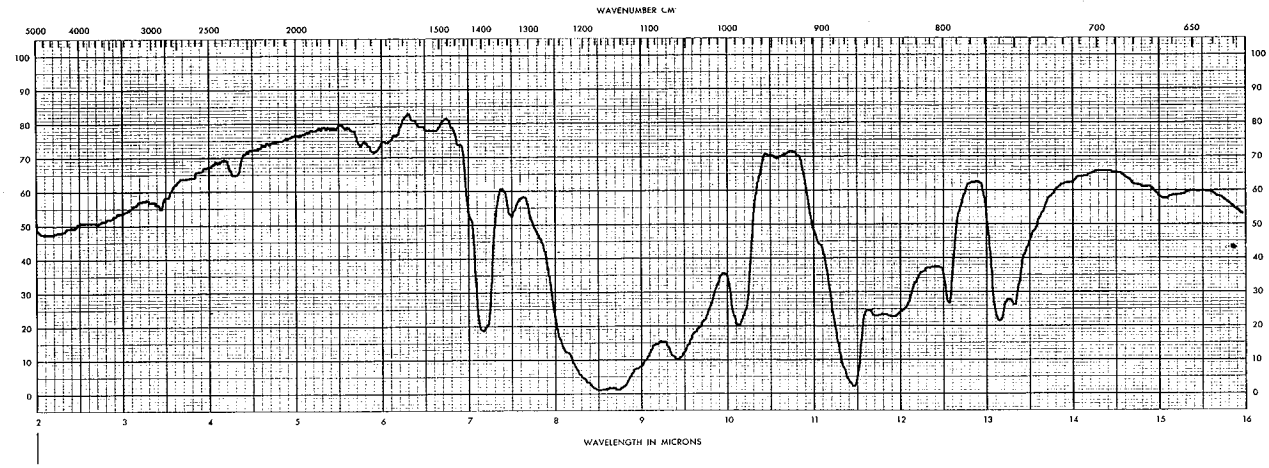


Figure 10. Infrared Spectrum of $C_3F_7OCF{=}CF_2/CH_2{=}CF_2$ Copolymer (ATR, 3 Reflections, 57°)

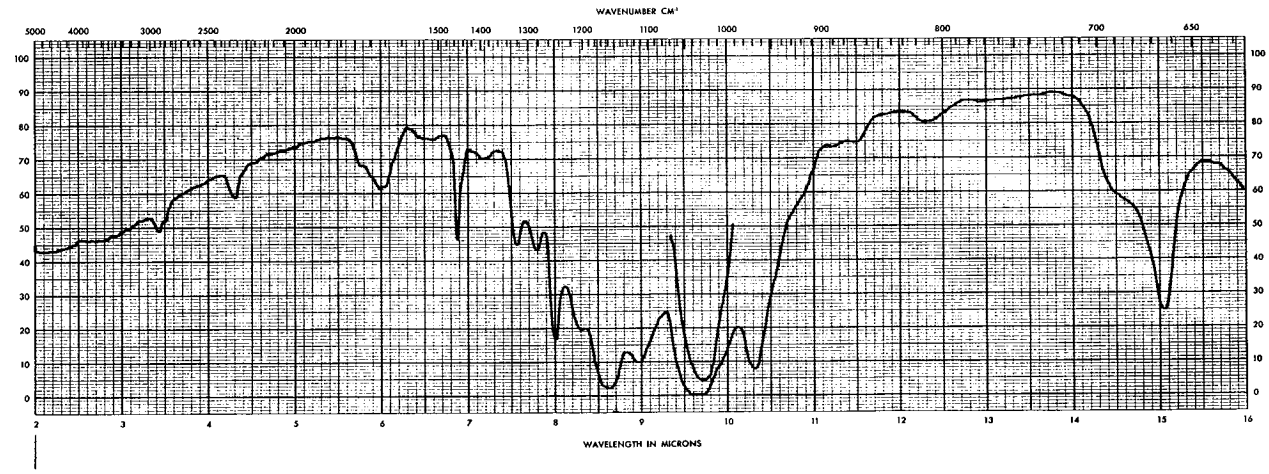


Figure 11. Infrared Spectrum of CF_3CHO/C_2F_4 Copolymer (ATR, 3 Reflections, 62°)

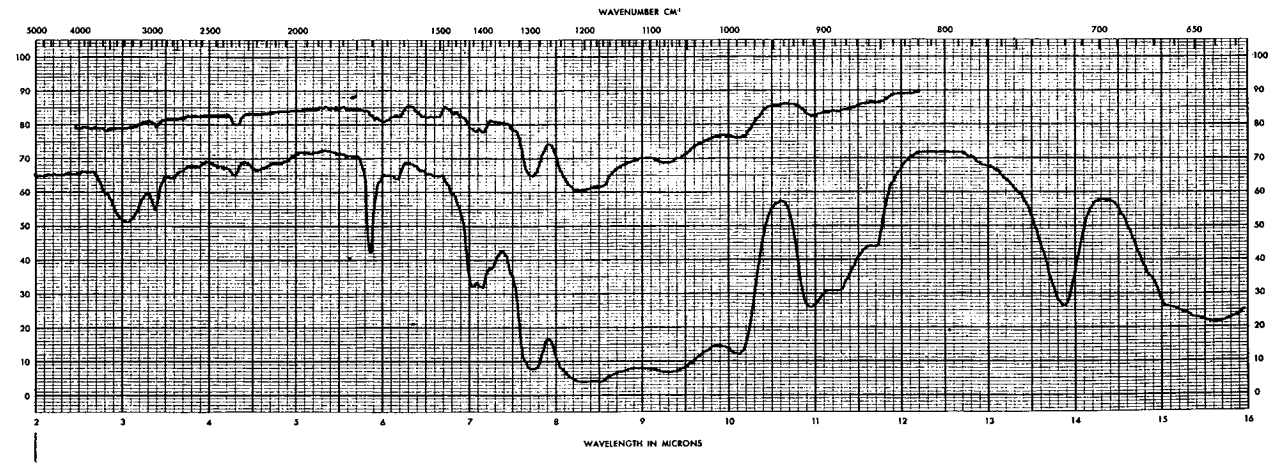


Figure 12. Infrared Spectrum of a Low Molecular Weight Poly(trifluoroacetaldehyde)

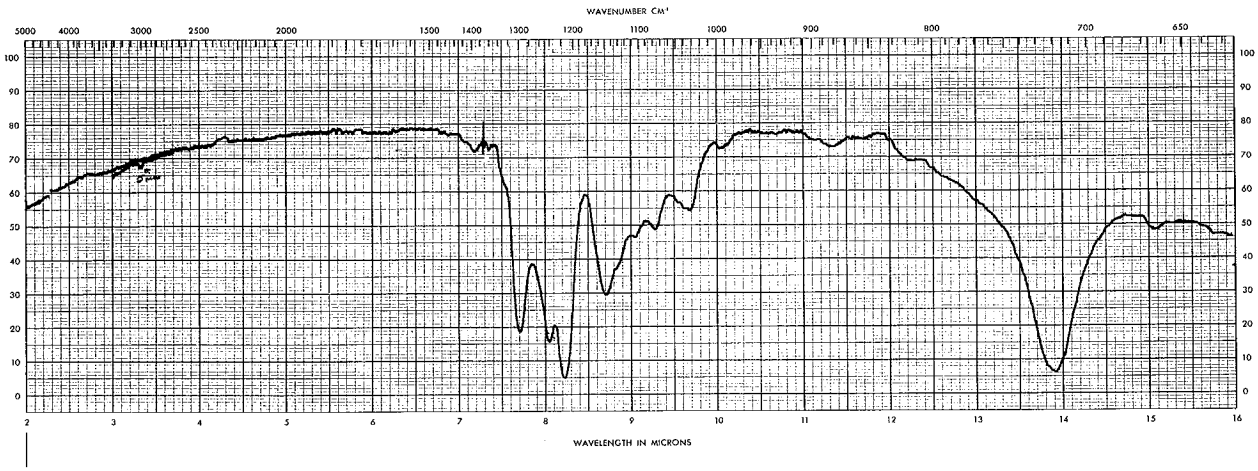


Figure 13. Infrared Spectrum of $CF_3OCHFCFClOCF_3$ (gas, 2 and 5 mm.)

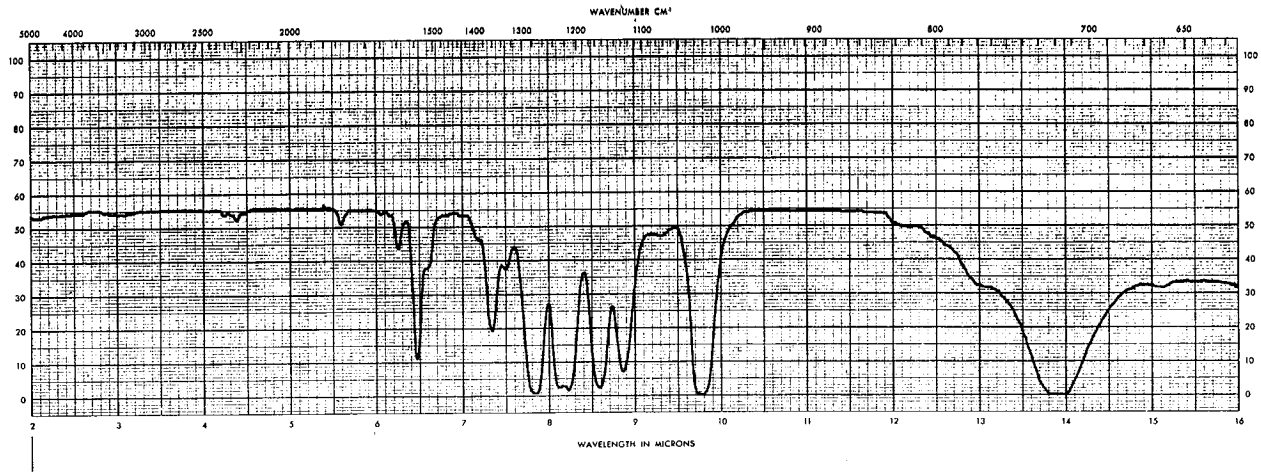


Figure 14. Infrared Spectrum of $CF_3\overline{CFCF_2O}$ (gas, 20 mm.)

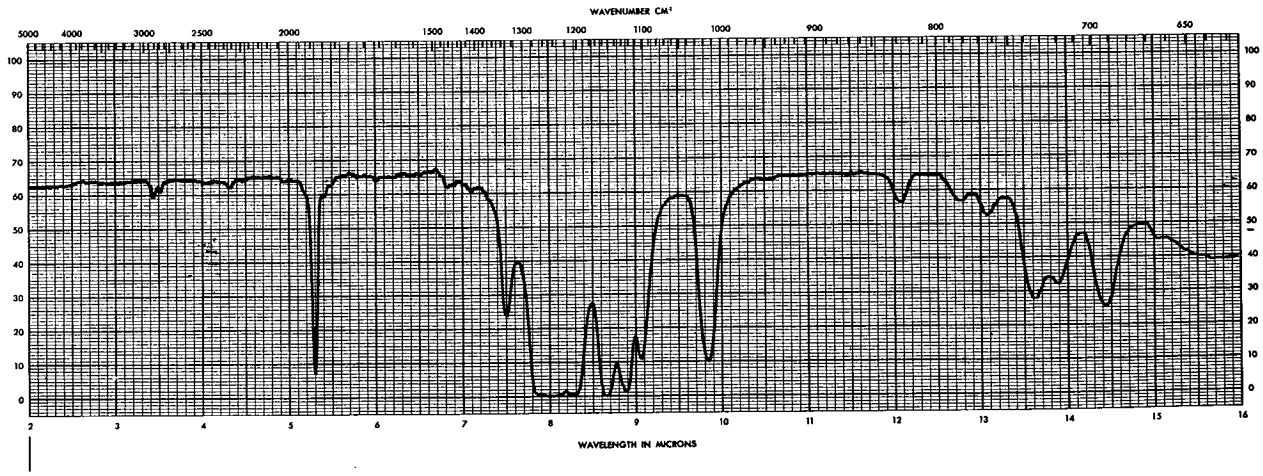


Figure 15. Infrared Spectrum of $C_2F_5OCF(CF_3)COF$ (gas, 10 mm.)

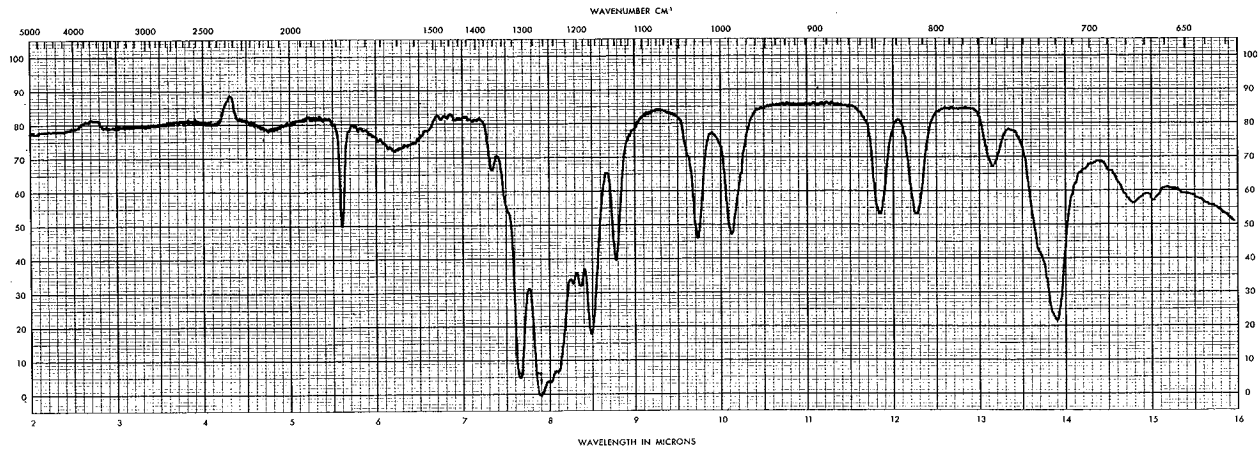


Figure 16. Infrared Spectrum of $C_2F_5COCF(CF_3)_2$ (gas)

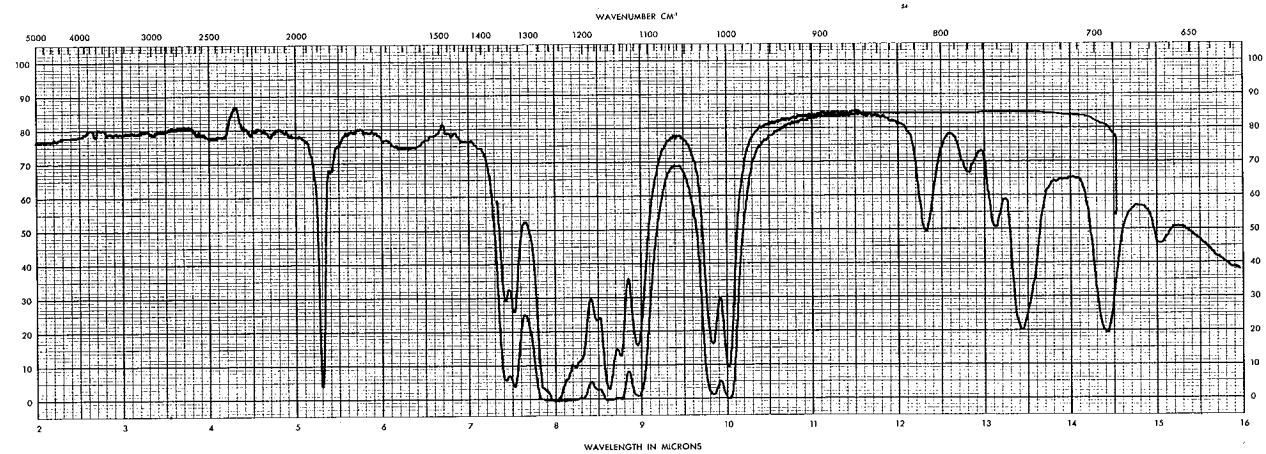


Figure 17. Infrared Spectrum of $C_3F_7OCF(CF_3)COF$ (gas)

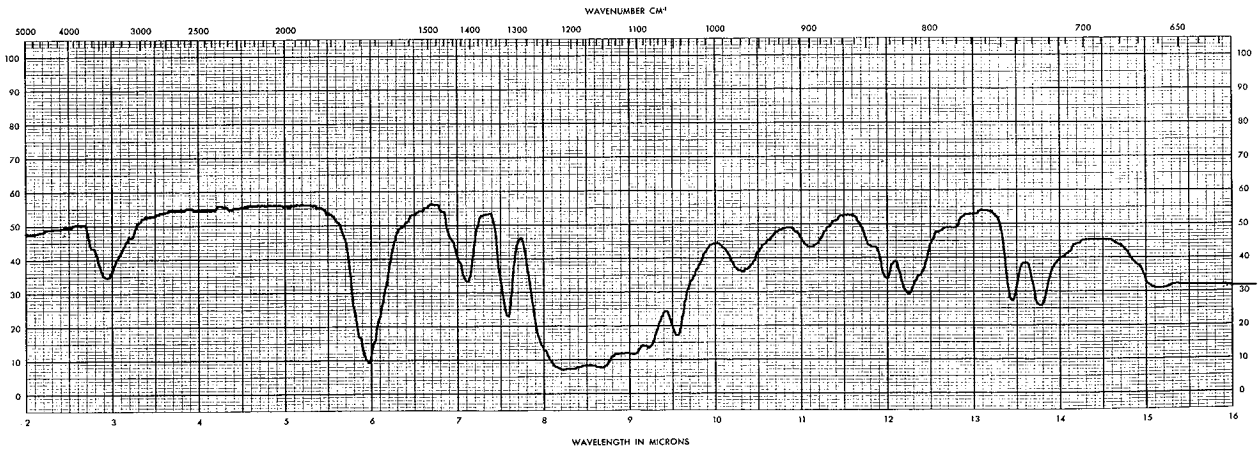


Figure 18. Infrared Spectrum of $C_2F_5OCF(CF_3)COONa$ (Kel-F mull)

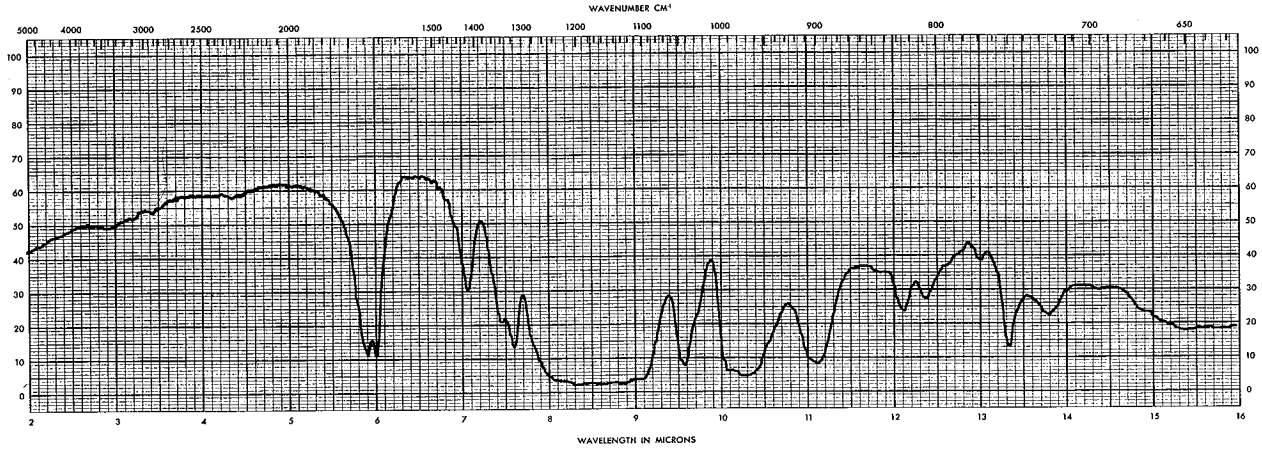


Figure 19. Infrared Spectrum of $C_3F_7OCF(CF_3)COONa$ (Kel-F mull)

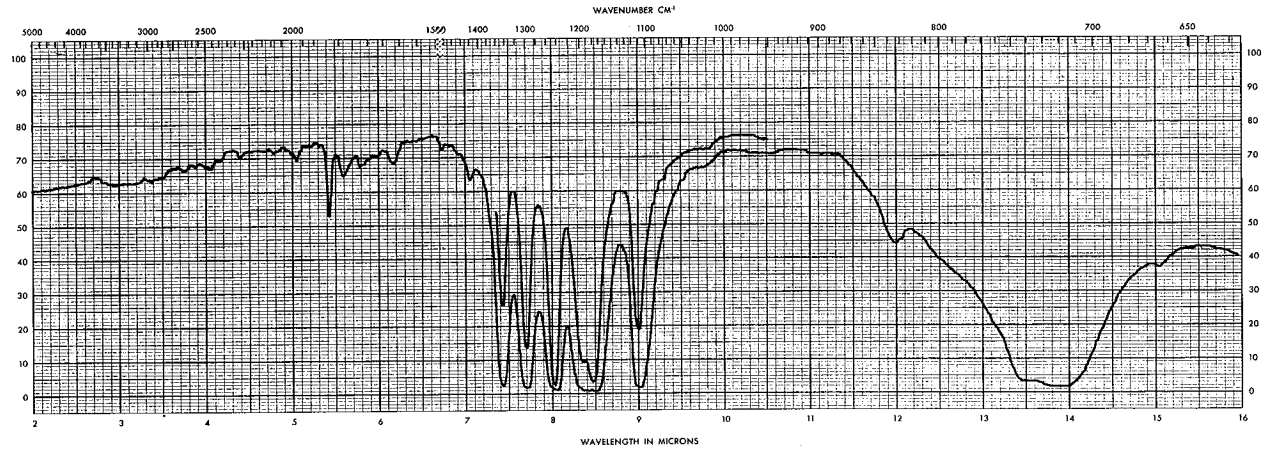


Figure 20. Infrared Spectrum of $C_2F_5OCF=CF_2$ (gas, 2 and 9 mm.)

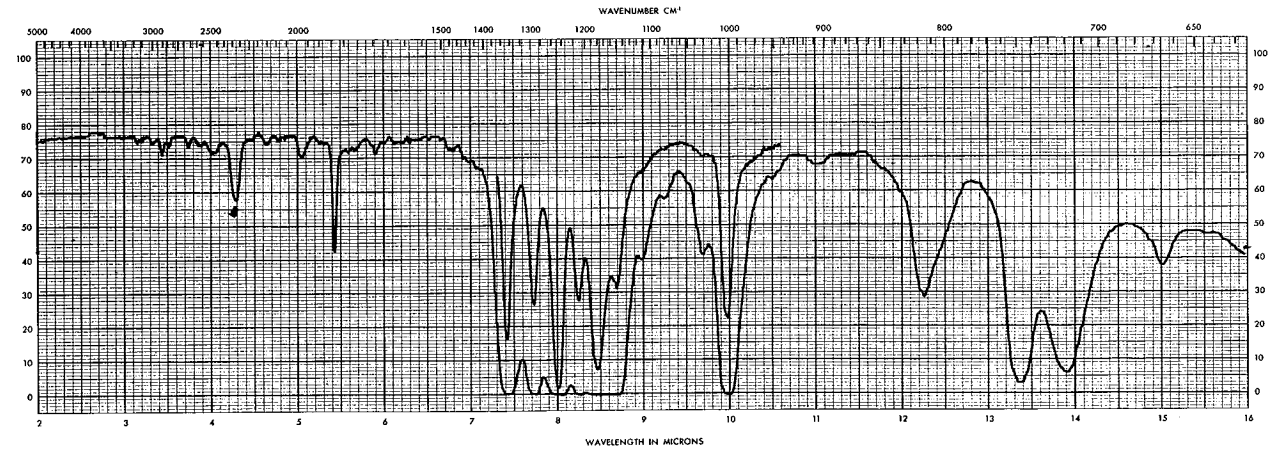


Figure 21. Infrared Spectrum of $C_3F_7OCF=CF_2$ (gas)

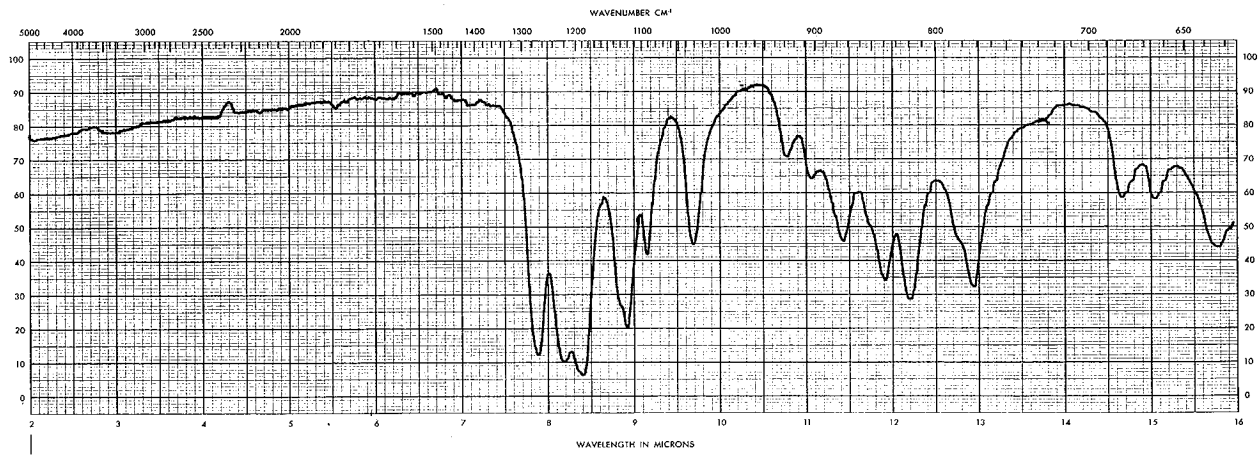


Figure 22. Infrared Spectrum of $CF_3OCCl_2CFCl_2$ (liquid)

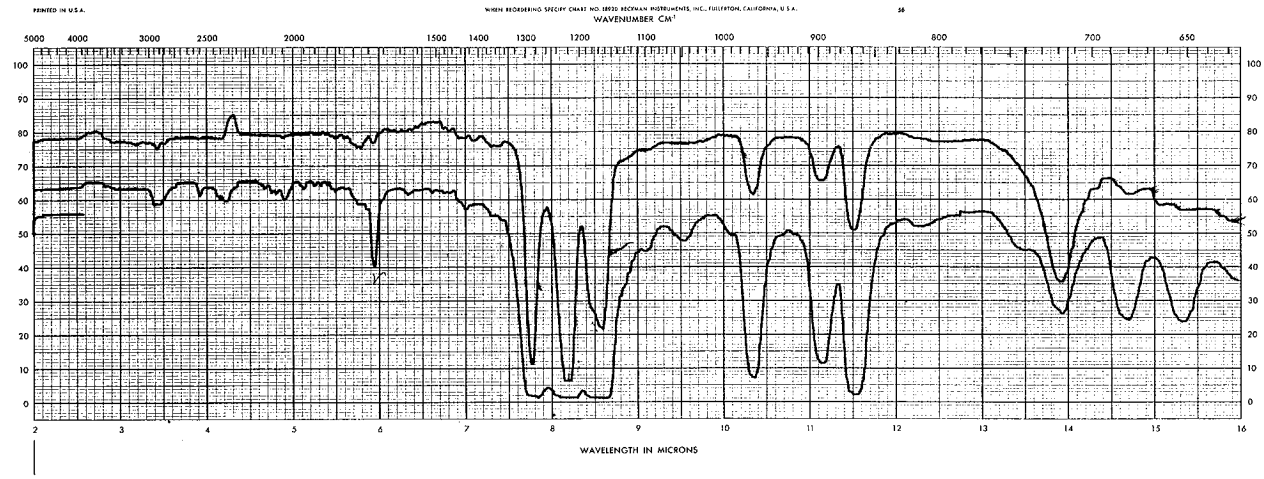


Figure 23. Infrared Spectrum of a 60/40 Cis/Trans Mixture of $CF_3OCCl{=}CFCl$ (gas, 5 and 25 mm.)

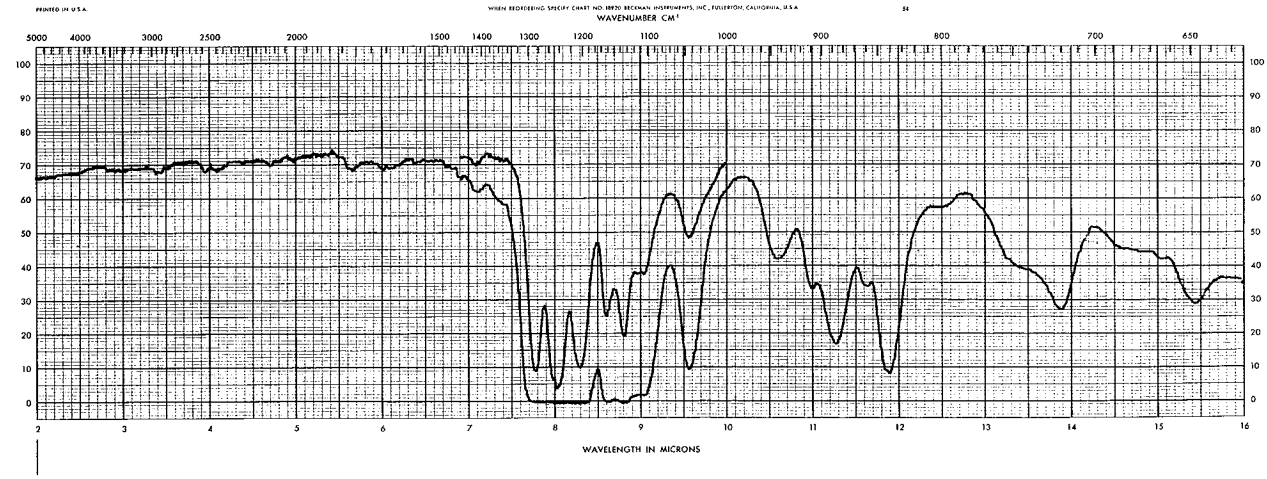


Figure 24. Infrared Spectrum of $(CF_3O)_2CClCF_2Cl$ (gas)

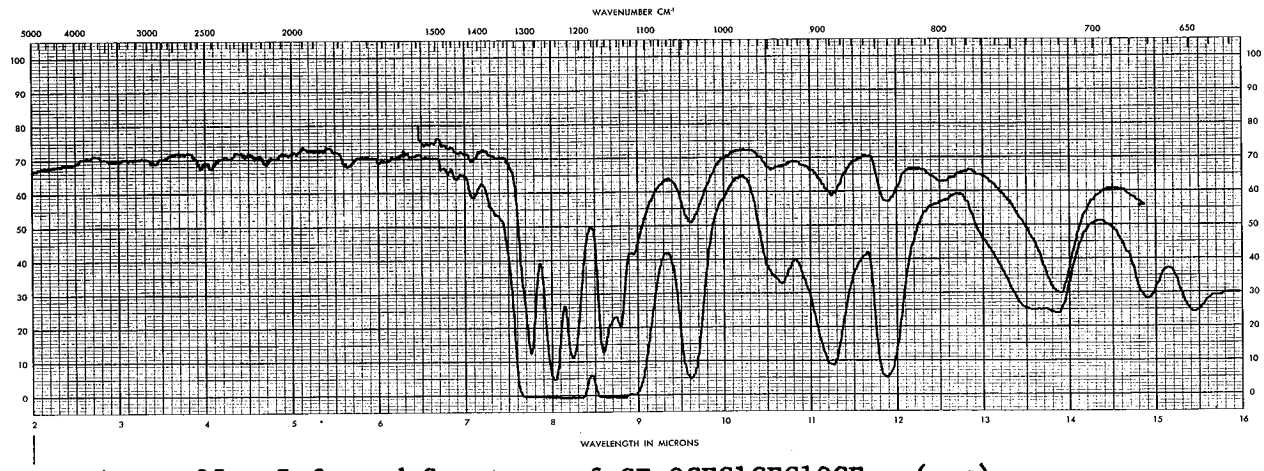


Figure 25. Infrared Spectrum of $CF_3OCFClCFClOCF_3$ (gas)

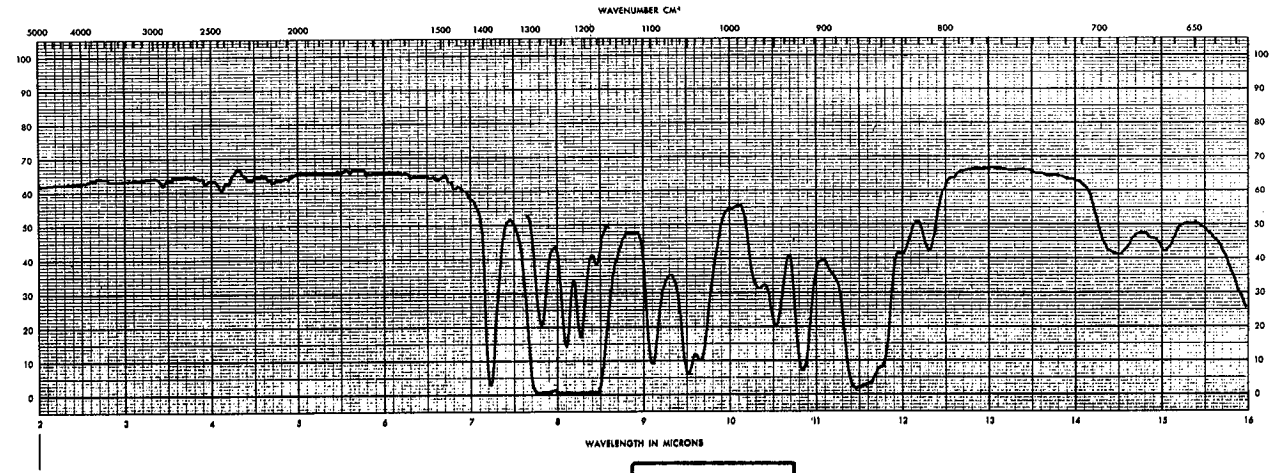


Figure 26. Infrared Spectrum of $\overline{CF_2CF_2CFClCClOCF_3}$
(3 and 20 mm.)

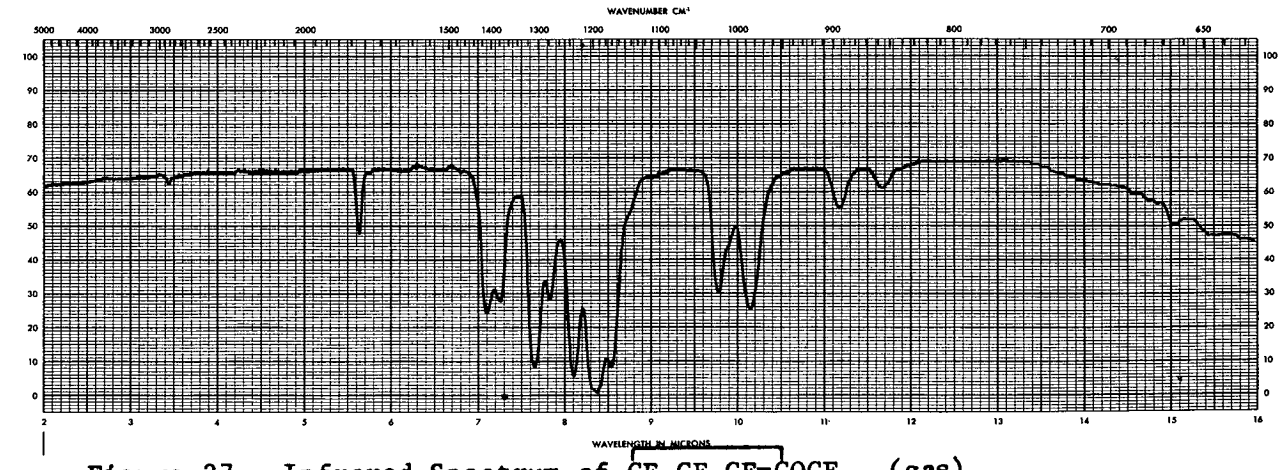


Figure 27. Infrared Spectrum of $\overline{CF_2CF_2CF{=}COCF_3}$ (gas)

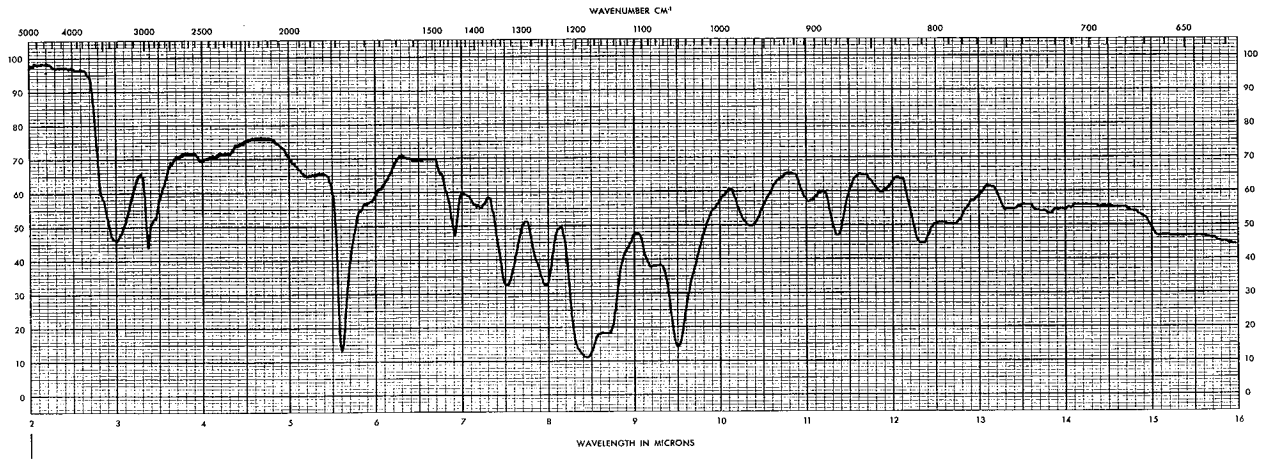


Figure 28. Infrared Spectrum of $HOOCCF_2CF_2COOCH_3$ (liquid)

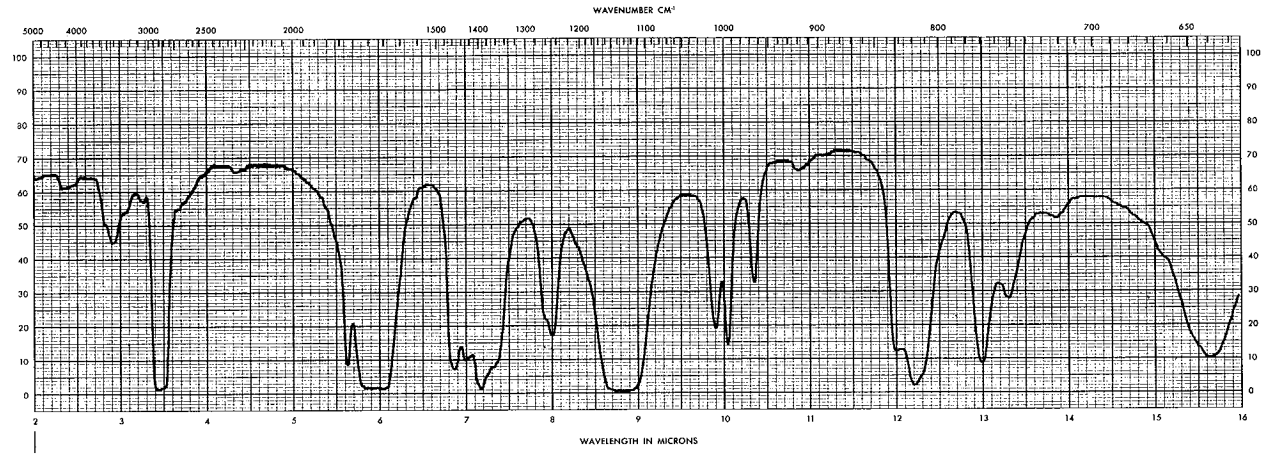


Figure 29. Infrared Spectrum of $NaOOCCF_2CF_2COOCH_3$ (Nujol mull)

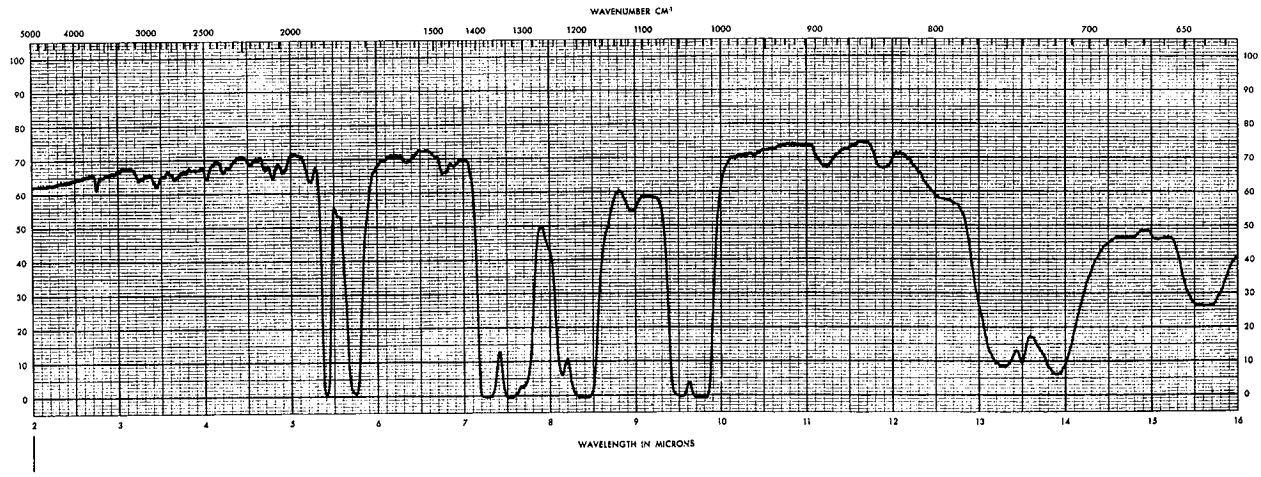


Figure 30. Infrared Spectrum of $CF_2{=}CFCOF$ (gas)

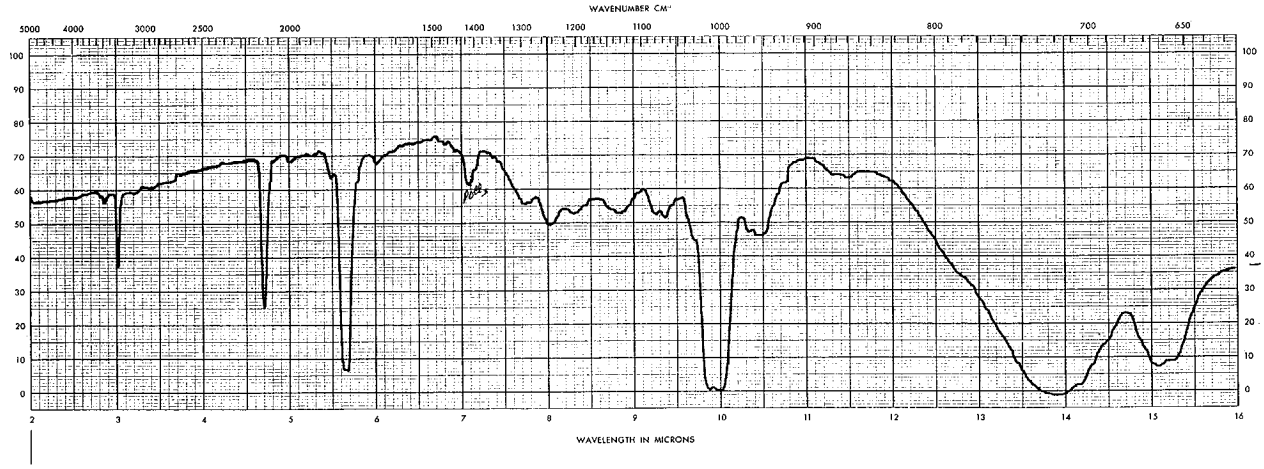


Figure 31. Infrared Spectrum of HC≡CCOCL (gas, 15 mm.)

APPENDIX

ANNOTATED BIBLIOGRAPHY

May, 1965 to April, 1966

INTRODUCTION

This bibliography was prepared from references obtained mainly from Chemical Abstracts but contains, in addition, references taken from a number of primary sources. Major emphasis was placed on references to fluorine-containing monomers and polymers and to thermal properties of all classes of polymers.

In past Annual Summary Reports references covered from 1957 to the date of the report. For the sake of brevity and to eliminate the need for duplicating earlier references, the present bibliography covers only the period of this report - May, 1965 to April, 1966.

As in the past, the great number of references in the categories covered necessitated selecting references which were considered to be of most significance to the present investigation. The choice of references is somewhat subjective, but it is felt that the cross-section given is a useful representation of the literature to date.

The references listed have been categorized with respect to the general subdivisions shown below. Once again for the sake of brevity no cross-referencing has been done, hence, where a paper was concerned with more than one subdivision the reference, in general, was placed in the category of greatest importance. Copolymers were placed in the earliest listed monomer category with the exception of the vinyl ethers and thioethers, the copolymers of which were included under the main heading of vinyl ethers.

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APPENDIX

Annotated Bibliography May, 1965 to April, 1966

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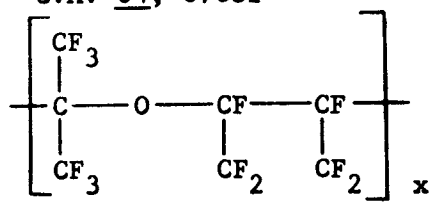

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